CADMIUM REMOVAL BY CHITOSAN

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of

MASTER OF TECHNOLOGY

By

INDRA NAND JHA

to the

DEPARTMENT OF CIVIL ENGINEERING

# INDIAN INSTITUTE OF TECHNOLOGY KANPUR

APRIL, 1984

CERTIFICATE

Certified that the work presented in this thesis entitled "Cadmium Removal by Chitosan" by Shri Indra Nand Jha has been carried out under my supervision and has not been submitted elsewhere for a degree.
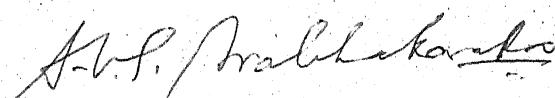
A.V.S. Prabhakara Rao
Professor
Department of Civil Engineering
Indian Institute of Technology
Kanpur.

April, 1984.

ACKNOWLEDGEMENTS

I would like to express my most sincere appreciation to Dr. A.V.S. Prabhakara Rao for his valuable advice, encouragement, suggestions and guidance which led to the successful completion of this work.

I am extremely grateful to Dr. Malay Chaudhuri, Dr. C. Venkobachar and Dr. (Mrs.) Leela Iyengar for their constant encouragement and assistance throughout my M.Tech. period. I am very much indebted to Dr. Vinod Tare for his valuable suggestions and help throughout my work.

I shall be failing in my duty if I do not avail this opportunity for thanking all those well wishers of mine who have given great inspirations to me in completing this work. The important of these personalities include S/s S.C. Prasad, V.S. Prasad, A.K. Dutta, Venky, Bhuwan, Kiran, K. Samy, Sarat, Jain, Amitabh Chakraborti, Sanjeev, Bhaskar, Satyanarayana, Prasad (Mrs.), Suchita and Rashmi.

My deep thanks will always remain towards Shri S.C. Barathwal of ACMS for helping me in the analysis of cadmium by A.A.S. I express my thanks to S/s R.C. Adhikari, A. Hassan, S.N. Mishra, Vijay, Indradev and Nek Ram Sahu for their help.

Lastly, I am grateful to my wife, sons and other members of my family who largely contributed to completion of this work by gladly suffering my neglect and lack of attention towards them, during the period of this study.

- I.N. Jha

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Cadmium in water is highly toxic and a potential hazard to aquatic, animal and human life. Much effort is made to develop efficient processes for cadmium removal from water and wastewater. Activated carbon seems to be effective in removing cadmium but it is expensive. Chitin is a structural polysaccharide of crabs, shrimp and shell fish. Chitosan prepared from chitin is reported to have good adsorption properties.

The adsorption of cadmium by chitosan was investigated to obtain information on cadmium removal from aqueous systems. Quantitative removal of cadmium from solution was obtained with chitosan. The adsorption of cadmium by chitosan was very rapid during the first 15 minutes. It was affected by pH of the solution, initial concentration of cadmium, chitosan to cadmium ratio, temperature and size of the chitosan particle. The batch sorption kinetic data fitted in the first order reversible reaction. The sorption equilibria data appeared to fit the Freundlich isotherm. The sorption of cadmium appeared to be similar to pore diffusion process as indicated by various experiments conducted to find out the rate limiting step, though other mechanisms might also be involved.

The mechanism of sorption was tried to relate with zero point of charge (pH_{zpc}). Presence of zinc and EDTA

depressed the cadmium uptake capacity of chitosan. However, presence of total ionic strength, chloride and calcium did not influence the cadmium uptake capacity of chitosan. Desorption of cadmium-chitosan system indicated ion-exchange nature of the sorption reaction apart from possible contributions from other mechanisms. First cycle of regeneration was complete by hydrochloric acid but it reduced subsequent cadmium uptake capacity of chitosan. Chitosan was dissolved to some extent in hydrochloric acid used for regeneration.

Down flow column studies showed the practical applicability of chitosan for removing cadmium. It reduced cadmium from an initial concentration of 5 mg/l to zero effluent concentration.

1. INTRODUCTION

The presence of toxic metals in potable waters, streams, domestic wastewater and industrial effluent is a matter of serious concern because of their adverse effect on water consumers, wastewater treatment systems or the biological system of water-bodies. The toxic metals include copper, chromium, cadmium, zinc, arsenic, silver, mercury, barium, selenium, lead and nickel. Among these heavy metals, cadmium has focussed our attention as a serious environmental contaminant. Extensive information exists on the acute and chronic effects of cadmium in man and experimental animals (Ryan et. al., 1982; Lauwerys, 1979).

Cadmium has found widespread use, mainly in metal finishing, metallurgical alloying, ceramics, photography, electrical applications, chemical industries and lead mines. These industries serve as a major source of cadmium pollution. Cadmium is used as a protective coating on iron, steel and copper. Cadmium sulfide is used in painting because it gives pigments a greater stability. Cables and welding electrodes coating is done by cadmium alloys of several metals. Variation in raw waste concentrations of cadmium among various plants is shown in Table 1.1 (Controlling Pollution of Metal Products, US EPA 1977).

The toxic nature of cadmium (Friberg et.al., 1974) is well known. It is generally taken up in the human body through gastriointestinal tract. As a result of contaminated

diet in industrialized countries, the cadmium body burden in middle age can be within five fold of the levels known to give early long term effects (Hammons et.al., 1978). Chronic cadmium exposure led to widespread proteinuria and in extreme cases Osteomalacia (Itai-Itai) in contaminated areas of Japan. Cadmium has been also classed as a probable human-carcinogen - with a high degree of supporting experimental and epidemiological evidence (IARC, 1980). The hazards produced through the irrigation using the cadmium-polluted water are additional.

Because of these health hazards, the levels of cadmium in drinking water supplies and industrial effluents must be reasonably low. The upper limit for cadmium in drinking water in India, U.S. and many other countries has been maintained at 0.01 mg/1 (Manual on Water Supply and Treatment,1976; NIPDWR, 1976).

The EPA effluent limitations for cadmium in the metal-finishing industry is 0.1 mg/1.

Many procedures have been developed for the removal of cadmium from aqueous solutions. Major treatment methods recently being suggested or employed for cadmium removal include hydroxide, carbonate and sulfide precipitation, Kastone process, ion exchange, adsorption, cementation, and reverse osmosis. The selection of a particular method depends mainly upon economic factors and effluent quality conditions required.

Of all treatment processes listed above, the adsorption process with proper adsorbents and under optimum operational

conditions, is an efficient separation process for solute removal. Again, the separation of the adsorbent, loaded with the adsorbate from the liquid phase, can be easily obtained, thus making adsorption an appealing method. Many sorbents like activated carbon, discarded automotive tires, serpentine mineral, starch Xanthate, coal and crushed coconut shell have been utilised for the removal of cadmium. Various agricultural products such as bark, peat moss and straw have also been tried to as sorbents for cadmium removal. Chitosan, a natural polymer, has shown positive response towards metal-binding capacity in some recent investigations. Chitin is the structural polysaccharide of crab shells and other crustaceans and is available from the waste materials of fish canning industries. Hydrolysis of chitin produces chitosan which is a very good adsorbent and is used for various purposes including binding enzymes. The purpose of the present study is to find out the adsorption potential of chitosan for the removal of cadmium.

Table 1.1*

Raw Waste Concentrations of Cadmium
(Variations among plants)

Sub-category	Minimum mg/l	Maximum mg/l	Mean mg/l
1. Casting and molding	0.002	0.443	0.044
2. Mechanical material removal	0.002	61.0	2.4
3. Metal forming (except plastics)	0.002	0.43	0.064
4. Physical property modifications	0.003	0.012	0.006
5. Assembly operations	0.002	60.9	1.3
6. Chemical-electro-chemical operations	0.002	0.029	0.011
7. Material coating	0.002	60.9	2.1
8. Smelting and refining	0.008	5.8	0.8
9. Molding and forming (plastics)	0.002	0.002	0.002

* From controlling pollution from the manufacturing and coatings of metal products, EPA 1977).

2. LITERATURE SURVEY

2.1 Cadmium

2.1.1 General:

Two German investigators, Strohmeier and Hermann discovered cadmium independently and almost simultaneously in 1817.

The use of cadmium on an appreciable scale received attention since the beginning of the current century. The specific properties of cadmium are employed in a number of industries. The chief use of cadmium is in electroplating (cadmium plating) and in the production of low-melting alloys.

Cadmium is a rare metallic element, and falls in group IIB of the Periodic Classification between zinc and mercury. Its chemical behaviour differs in significant ways from that of both these elements, although it shows greater similarities to zinc (Aylett, 1979). Its atomic weight is 112.41 and its atomic number is 48. It is a divalent metal with distinctly basic properties (Chizhikov, 1966).

2.2 Cadmium in the Environment

Cadmium is a relatively rare but widely distributed element. It has an estimated crustal abundance of between 0.15 µg/g (Weast, 1969) and 0.2 µg/g and thus occurs in sixty-seventh position in order of relative abundance (Aylett, 1973). Range of cadmium concentration in soil (non-polluted) varies from 0.01 to 0.7 µg/g with an estimated mean soil content of 0.2 µg/g.

The main sources of variation in the cadmium contents
of unpolluted soils are the small variations in the inherent
composition of the soil material and the inputs of metal from
fertilizers, manures, agricultural chemicals and general
atmospheric pollution. With regard to inputs from extraneous
sources, the contributions from phosphatic fertilizers and
sewage sludge are the most important, but localised atmos-
pheric pollution or large application of sewage can elevate
the cadmium content of soils sufficiently for them to be
considered 'polluted'. Copper, lead, nickel and zinc sulphide
ore smellters are conspicuous sources of cadmium and vege-
tation and soils can be significantly contaminated upto 40 Km
downwind. Buchauer (1973) reported a linear relationship
between the log of cadmium deposited and the distance from
the smelter. Concentrations of upto 1700 µg/g Cd have been
found in polluted top soil in the vicinity of zinc smelter
(Buchauer, 1973). The dispersion of this element from
metallurgical industries such as electroplating, can be by
emission into the atmosphere in fumes and transported as
particles of cadmium oxide, deflation of cadmium-containing
'dust' or the flow of liquid effluents containing cadmium
in solution or suspension into water courses or sewage
systems.

Cadmium entering the soil constitutes a more lasting
form of pollution, since uptake by plants can continue long
after the direct airborne pollution has ceased. A small
proportion of the airborne particulate cadmium which is

deposited and retained on plant surfaces, is absorbed via the leaves and some of that reaching the soil will be taken up through the roots, but majority of the pollutants will remain on the leaf surfaces. Plants collected near major highways were reported by Lagerwerff and Specht (1970) to contain higher concentrations of cadmium than those collected many meters from the roadway. Aerial deposition of cadmium containing dust from motor vehicle tyres and lubricants can account for some of the elevated cadmium levels of plant near highways.

Heavy metals are considered to be main factor limiting the agricultural use of sewage sludges. Cadmium concentrations in sewage sludge from Western Europe and North America range from 1 to 3650 μg Cd/g in the dry matter (Peterson and Alloway, 1969).

An additional source of cadmium are the pipes through which drinking water passes. Zinc galvanized iron pipe in which cadmium is contaminant has the potential of imparting cadmium to water.

The principal source of cadmium in the normal human diet would appear to be from food rather than air or water (Fleischer et.al., 1974). This may not be true for smokers, as tobacco can contain a high concentration of cadmium which is inhaled in the smoke. Estimates of the cadmium intake from foodstuffs are about 20-50 μg/day (Fleischer et.al., 1974). Municipal sludges, wastewater and phosphate fertilizer applied to agricultural lands are potentially important

sources of cadmium entry into the human food chain (CAST, 1976). Aquatic food species, including fish, crabs, oysters and shrimps, bioconcentrate Cd. Milk is an important source of cadmium to the infant and child. Breast milk has been shown to have a median cadmium content of 11.1 μg/l (Pinkerton et.al., 1972). Median cadmium values in cow's milk were found to be 26 μg/l.

Ambient air and drinking water contribute relatively little to the average daily intake.. Irrespective of the route of entry, Cd is principally stored in the liver and kidneys with higher levels initially found in the liver (Gunn and Gould, 1957; Kanwar et.al., 1980). The accumulation in liver and kidneys seems to be mainly dependent on the storage of Cd in association with the Cd-binding protein metallothionein (Friberg et.al., 1974). Total body burden Cd in humans increases with age (Friberg et.al., 1974).

Cadmium occurs naturally in the aquatic environment and does not appear to be a potential hazard in the open oceans. Its chemical speciation in natural waters may be complex and can greatly influence the rate and the extent of accumulation both in fresh water and marine organisms.

Organisms accumulate cadmium in their tissues with the filter feeders (bivalves and crustacea) showing the greatest concentration factors. While the majority of examples of organisms with high cadmium concentrations in their tissues can be equated with mining and/or industrial pollution, certain species, such as sea — Skaters and

distant ocean sea-birds have accumulated cadmium from unknown sources, suggesting geochemical factors may be responsible. Cadmium is taken up by a passive diffusion process, influenced by the chemical species presented to the organism.

2.3 Toxicity and Biological Effects of Cadmium

Cadmium has come to be recognized as a highly toxic and dangerous environmental pollutant. Exposure to cadmium may cause a wide variety of acute and chronic effects. Drinking water and food constitute the principal environmental source of cadmium for the non-smoking human population. The absorption of Cd from the lung occurs at a substantially higher rate (10-14 percent) than that from the gastriointestinal tract (3-6%) (Friberg et.al., 1971). Smoking 20 cigarettes per day is equivalent to ingesting 25 μg Cd from food. Irrespective of the route of entry, Cd is principally stored in the liver and kidneys with higher levels initially found in the liver (Kanwar et.al., 1980). In humans, about one-third of the life-time burden of cadmium accumulates within 3 years of birth (Henke et.al., 1970). Most of the cadmium remains in plasma for the first few hours after administration (Nomiyama, 1973).

The toxicity of the metal and its compounds in the human system has been mainly attributed to its strong binding with sulphur of a SH-group (e.g. cystein residues) in enzymes leading to blockade of enzymic activity of thiol group (Pandey, 1982). Metallothionein is an inducible metal-binding protein which has been implicated as a possible mediator of cadmium toxicity (Nordberg, 1978).

The principal accute manifestations observed in man are gastriointestinal disturbances following ingestion and chemical pneumonitis following inhalation of cadmium oxide fume. In animals, acute administration of cadmium also can produce toxic effects in other organs (Cardiovascular system, kidney, liver, nervous system, haematopoietic system, pancreas, immunological system, reproductive system) but the relevance of these effects for man remains doubtful. Long term human exposure to cadmium has been linked with the development of various signs and symptoms in particular: Lung insufficiency, renal disturbances, osteomalacia, anaemia, anosmia, yellow colouration of teeth and hypertension. A few studies also have suggested that cadmium could be carcinogenic in man (Lauwerys, 1979).

A specific disease known as 'itai-itai' in Japan has been attributed to cadmium. This occurred mainly in one area of Japan located along the Jintzy river and the areas where the soil was polluted by cadmium (Friberg et.al., 1974).

Usually the kidney is the organ (critical organ) which exhibits the first adverse effect following long-term excessive exposure to cadmium by inhalation or ingestion (Nordberg, 1978). Cadmium accumulates in the renal cortex where it produces morphological and functional changes. Cadmium concentrations of between 200 and 300 $\mu g/g$ wet weight generally result in renal dysfunction, with the 200 $\mu g/g$ level being the most widely accepted number at which the first signs of β_2-microproteinuria occur.

In animals subcutaneous or intramuscular injection can induce cancer. It has been shown that the injection of Cd metal or salt causes malignancies (Sarcoma) at the site of injection and testicular tumours distal to the injection site. Cadmium inhibits the ability of immune murine macrophages to destroy tumour cells at concentrations as low as 10^{-6} M (Nelson et.al., 1982). The half-life of Cd in the blood has been estimated to be about 3 months and from 8 to 30 years in the tissues of the liver, kidney and muscle (Elinder et. al., 1978). It is possible that chronic exposure of low, and presumably nontoxic, doses of the metal may, in fact, accumulate to levels that can have adverse effects on the immune system. Perry analyzed the concentration of trace metals in the urine of normal individuals and hypertension patients and found a strong correlation between illness and cadmium concentration levels.

2.4 Aquatic Chemistry of Cadmium

Cadmium in aqueous solution has a pronounced tendency to form soluble complexes with both organic and inorganic ligands. Dissolved cadmium in water may be present as free Cd^{2+} ion and in the form of complexes: inorganic: hydroxides, carbonates and chlorides, or organic, of diverse composition (Gardiner, 1974).

The equilibria pertaining to the hydroxy complexes of cadmium can be represented in terms of the stepwise formation of these species:

Table 2.1

Equilibrium Constants Used for Calculation of Cadmium
Distribution and Solubility Diagrams

Ligand	Log_{10} of Equilibrium constants				Conditions
	K_1	K_2	K_3	K_4	
OH^-	4.16	4.23	0.69	-0.32	Zero ionic strength, 25°C
Cl^-	1.32	0.90	0.09	-0.45	4.5 M $NaClO_4$, 25°C

Ligand	Overall Formation Constants				Conditions
	β_1	β_2	β_3	β_4	
OH^-	1.45×10^4	2.46×10^8	1.20×10^9	5.76×10^8	Zero ionic strength, 25°C
Cl^-	21.0	166.0	204.0	71.5	4.5 M $NaClO_4$, 25°C

$$Cd^{2+} + OH^- \rightleftharpoons CdOH^+ \quad ; \quad K_1 \qquad 2.1$$

$$CdOH^+ + OH^- \rightleftharpoons Cd(OH)_2 \quad ; \quad K_2 \qquad 2.2$$

$$Cd(OH)_2 + OH^- \rightleftharpoons HCdO_2^- + H_2O \quad ; \quad K_3 \qquad 2.3$$

$$HCdO_2 + OH^- \rightleftharpoons CdO_2^- + H_2O \quad ; \quad K_4 \qquad 2.4$$
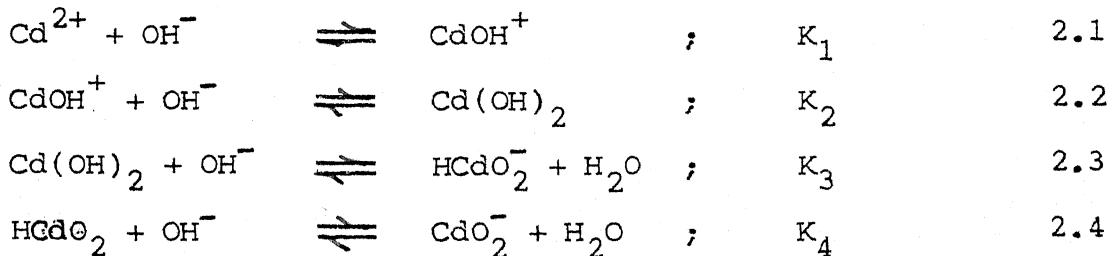
Values for the stepwise formation constants, K_1 through K_4,
are given in Table 2.1. For reasons of convenience it is
customary to replace the stepwise formation reactions by
overall formation reactions. The latter are mathematical
representations only and do not depict elementary reaction
steps. Stepwise formation constants $K_1 \ldots K_4$ and overall
formation constants $\beta_1 \ldots \beta_4$ are related by

$$\beta_1 = K_1$$

$$\beta_2 = K_1 \cdot K_2$$

$$\beta_3 = K_1 \cdot K_2 \cdot K_3$$

$$\beta_4 = K_1 \cdot K_2 \cdot K_3 \cdot K_4$$

$$Cd^{2+} + OH^- \rightleftharpoons CdOH^+ \qquad ; \qquad \beta_1 \qquad\qquad 2.5$$

$$Cd^{2+} + 2OH^- \rightleftharpoons Cd(OH)_2 \qquad ; \qquad \beta_2 \qquad\qquad 2.6$$

$$Cd^{2+} + 3OH^- \rightleftharpoons HCdO_2^- + H_2O \quad ; \qquad \beta_3 \qquad\qquad 2.7$$

$$Cd^{2+} + 4OH^- \rightleftharpoons CdO_2^{2-} + 2H_2O \; ; \qquad \beta_4 \qquad\qquad 2.8$$
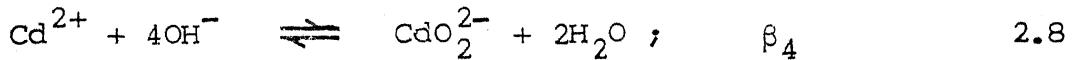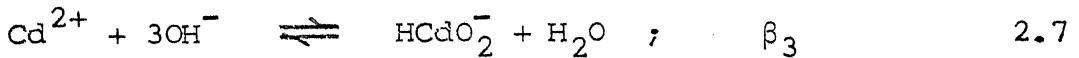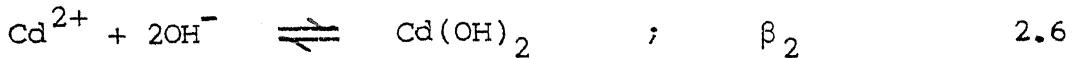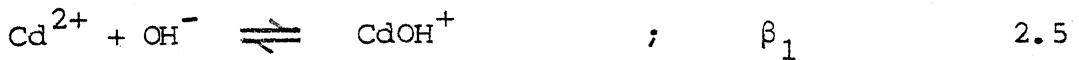
A mass balance on soluble cadmium species with a total of C moles/l as Cd, therefore, is given by

$$C = [Cd^{2+}] + [CdOH^+] + [Cd(OH)_2] + [HCdO_2^-]$$
$$+ [CdO_2^{2-}] \qquad\qquad 2.9$$

Substituting in terms of the formation constants from Equations 2.5 through 2.8 gives

$$C = [Cd^{2+}] (1 + \beta_1 [OH^-] + \beta_2 [OH^-]^2 + \beta_3 [OH^-]^3$$
$$+ \beta_4 [OH^-]^4) \qquad\qquad 2.10$$

If α is defined as the function of a particular species relative to the total analytic concentration then $[A] = \alpha_A \cdot C$ and the sum of α's over all species is 1:

$$\sum_{i=0}^{n} \alpha_i = \alpha_0 + \alpha_1 + \ldots + \alpha_n = 1 \qquad\qquad 2.11$$

The fraction of the individual solute species of cadmium then
may be calculated as a function of hydroxide concentration.
Thus α_n is independent of the cadmium concentration in solu-
tion.

$$\alpha_O = \frac{[Cd^{2+}]}{C}$$

$$= \frac{1}{1 + \beta_1 [OH^-] + \beta_2 [OH^-]^2 + \beta_3 [OH^-]^3 + \beta_4 [OH^-]^4} \qquad 2.12$$

$$\alpha_1 = \frac{[CdOH^+]}{C} = \beta_1 [OH^-] \alpha_O \qquad 2.13$$

$$\alpha_2 = \frac{[Cd(OH)_2]}{C} = \beta_2 [OH^-]^2 \alpha_O \qquad 2.14$$

$$\alpha_3 = \frac{[HCdO_2^-]}{C} = \beta_3 [OH^-]^3 \alpha_O \qquad 2.15$$

$$\alpha_4 = \frac{[CdO_2^{2-}]}{C} = \beta_4 [OH^-]^4 \alpha_O \qquad 2.16$$

The distribution of these species as a function of pH is
shown in Figure 2.1. The distribution diagram for cadmium
hydroxy complexes reveals that the species Cd^{2+}, $CdOH^+$,
$Cd(OH)_2$(aq) and $HCdO_2^-$ contribute increasingly to the solu-
bility of cadmium in the range of pH 7-12. The distributions
of species for cadmium chloride are presented in Figure 2.2.
In accord with this diagram, complexation by chloride ion
becomes a significant factor in solubility considerations
of systems containing greater than 10^{-3} M chloride. The
role of ammonia as a ligand appears rather insignificant
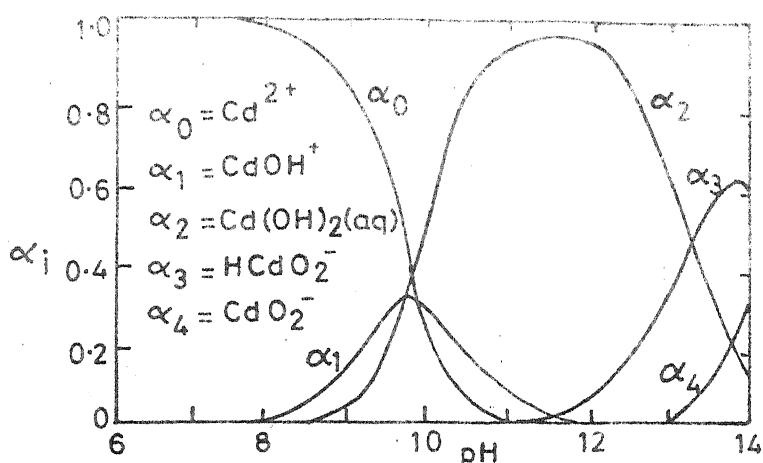
Fig. 2·1 Distribution Diagram for Cadmium Hydroxide Complex (Weber and Possett, 1974)

$\alpha_0 = Cd^{2+}$
$\alpha_1 = CdOH^+$
$\alpha_2 = Cd(OH)_2(aq)$
$\alpha_3 = HCdO_2^-$
$\alpha_4 = CdO_2^-$

$\alpha_0 = Cd^{2+}$
$\alpha_1 = CdCl^+$
$\alpha_2 = CdCl_2$
$\alpha_3 = CdCl_3^-$
$\alpha_4 = CdCl_4^{2-}$
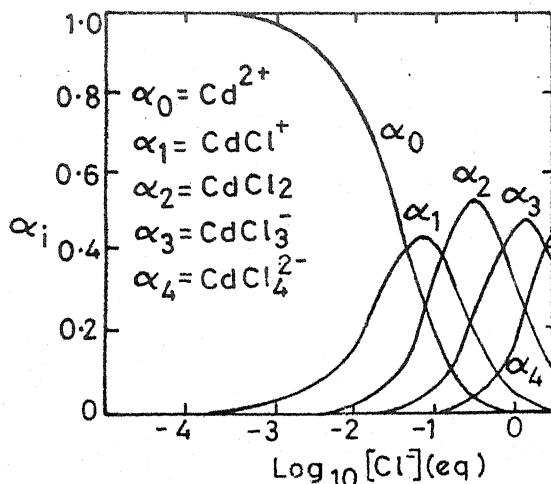
Fig. 2·2 Distribution Diagram for Cadmium Chloride Complex (Weber and Possett, 1974)
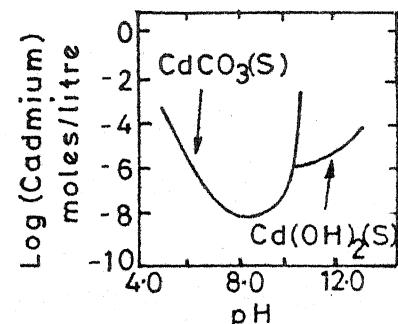
Fig. 2·3 Phase Diagram of Cadmium at $[CO_3^{2-}]$ total = 0·005M (Robhun, S. et. al. 1984)

considering its relatively low concentration in most natural waters and wastewaters.

The total concentration of dissolved cadmium, C, is the sum of all the forms of inorganic and organic ligands. Considering inorganic ligands only

$$C = Cd^{2+} \left[1 + K_1 [CO_3^{2-}] + K_2 [Cl^-] + K_3 [Cl^-]^2 + K_4 [Cl^-]^3 \right.$$
$$\left. + K_5 [Cl^-]^4 + \beta_1 [OH^-] + \beta_2 [OH^-]^2 + \beta_3 [OH^-]^3 \right] \qquad 2.17$$
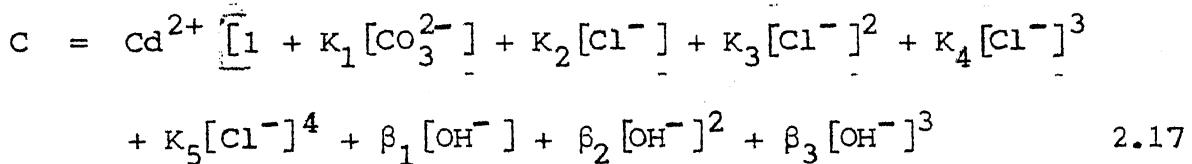
where K_1 is the formation constant of the carbonate complex $CdCO_3(aq)$, K_2-K_4 are the overall formation constants of chloride complexes: $CdCl^+$, $CdCl_2(aq)$, $CdCl_3^-$ and $CdCl_4^{2-}$, respectively. Of the four possible existing chloride complexes of cadmium $(CdCl_x)^{2-x}$, the dominant species are determined by the chloride ion concentration present.

2.4.1 Solubility Equilibria for Cadmium

The solubility of the metal hydroxide is defined by solubility products (K_s) and the equations relating the metal hydroxide solid species in equilibrium with soluble free metal ion or metal hydroxide species. The following equations may be used to describe the solubility of cadmium hydroxide

$$Cd(OH)_2 \ (s) \quad \rightleftharpoons \quad Cd^{2+} + 2OH^- \qquad K_{s}o \qquad 2.18$$

$$Cd(OH)_2 \ (s) \quad \rightleftharpoons \quad Cd(OH)^+ + OH^- \qquad K_{s}1 \qquad 2.19$$

$$Cd(OH)_2 \ (s) \quad \rightleftharpoons \quad Cd(OH)_2^o \qquad K_{s}2 \qquad 2.20$$

$$Cd(OH)_2 \text{ (s)} + OH^- \rightleftharpoons Cd(OH)_3^- \qquad K_{s}3 \qquad 2.21$$

$$Cd(OH)_2 \text{ (s)} + 2OH^- \rightleftharpoons Cd(OH)_4^{2-} \qquad K_{s}4 \qquad 2.22$$
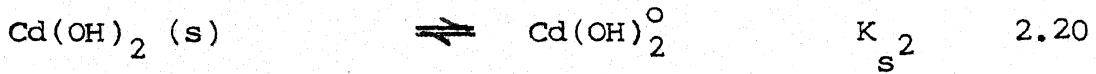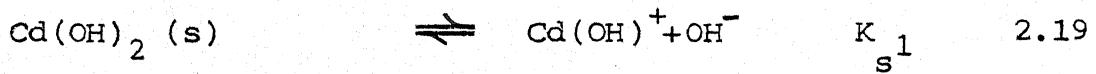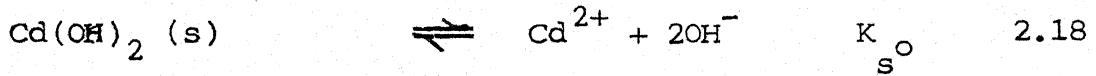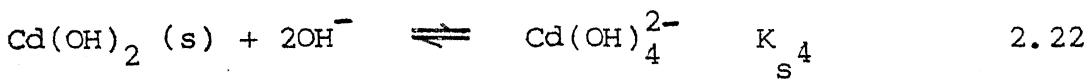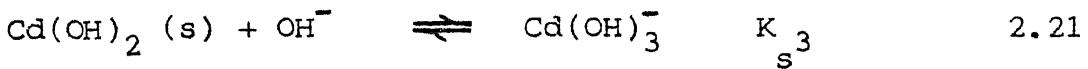
Each equation describes an equilibrium reaction between the solid phase $Cd(OH)_2$ (s), and a soluble species of the metal cadmium. The equilibrium position of each reaction is described by a solubility product constant K_s, as follows:

$$K_{s}o = [Cd^{2+}][OH^-]^2 \qquad 2.23$$

$$K_{s}1 = [Cd(OH)^+][OH^-] \qquad 2.24$$

$$K_{s}2 = [Cd(OH)_2^o] \qquad 2.25$$

$$K_{s}3 = [Cd(OH)_3^-][OH^-] \qquad 2.26$$

$$K_{s}4 = [Cd(OH)_4^{2-}][OH^-]^2 \qquad 2.27$$

Taking the logarithmic form and rearranging the following equations are obtained:

$$Log[Cd^{2+}] = Log K_s - 2pH + 28 \qquad 2.28$$

$$Log[Cd(OH)^+] = Log K_{s}1 - pH + 14 \qquad 2.29$$

$$Log[Cd(OH)_2^o] = Log K_{s}2 \qquad 2.30$$

$$Log[Cd(OH)_3^-] = Log K_{s}3 + pH - 14 \qquad 2.30$$

$$Log[Cd(OH)_4^{2-}] = Log K_{s}4 + 2pH - 28 \qquad 2.31$$

In each above equation, the term for log hydroxyl activity is substituted by the expression (pH - 14) based upon the self-ionization of water.

Each of Equations 2.28 through 2.31 may be plotted using appropriate solubility constants to define the cadmium hydroxide solubility curve in which cadmium is given by the summation of all metal species. The range of cadmium hydroxide solubility product constants for drawing the solubility diagram are presented in Table 2.2.

Table 2.2

Cadmium Hydroxide Solubility Product Constants

	Log of Solubility Product Constants					pH of Minimum Metal Hydroxide Solubility
	$K_{s}0$	$K_{s}1$	$K_{s}2$	$K_{s}3$	$K_{s}4$	
Cadmium (aged)	-14.4	-10.2	-6.0	-5.3	-5.6	
Cadmium (fresh)	-13.7	-9.5	-5.3	-4.6	-4.9	10.5

The aging process involves slow physico-chemical transformations within the freshly precipitated solid phase.

Cadmium carbonate solubility is a function of the equilibria between cadmium carbonate and cadmium metal species. This system is defined in terms of solubility products (K_s) for the specific cadmium carbonate. The

equilibrium expression, for solubility of cadmium carbonate, is defined as

$$\text{Log } Cd^{2+} = \log K_{sp} - \log CO_3^{2-} \qquad 2.32$$

The carbonate concentration is defined by three pH ranges, the dividing points of which are the two dissociation constants for carbonic acid, $K_1 = 10^{-6.3}$ and $K_2 = 10^{-10.3}$.

To completely define solubility for the cadmium carbonate system, hydrolysis of the cadmium ion to form stable cadmium hydroxide species must be considered. The solubility diagram is constructed by superimposing the diagram for the hydroxide system on that for the carbonate system at a particular total carbonate concentrations. Figure 2.3 shows a particular solubility diagram at total carbonate concentration of 0.005 M.

2.5 Removal of Cadmium from Water and Wastewater

Several methods are available for removing cadmium from water and wastewater, including precipitation as hydroxide (Jenkins et.al., 1964; Argo and Culp, 1972; Sorg et.al., 1978; Bhatia et.al., 1979), carbonate (Patterson et.al., 1977) and sulfide (Summary Report, EPA, 1980), ion exchange (Linstedt et.al., 1971), reverse osmosis (Hindin et.al., 1968), foam separation (Chou and Okamato, 1976) and adsorption (Netzer and Norman, 1973; Netzer et.al., 1974; Randall et.al., 1974; Wing et.al., 1975; Sunderesan et.al., 1978; Huang and Ostovic, 1978; Chaney and Hundemann, 1979; Huang and Smith, 1981; Larsen and Schierup, 1981; Huang and Wirth, 1982; Bhattacharya, 1983).

Patterson (1975) and Rouse (1976) have reviewed metal
removing techniques and suggested that the selection of
method was largely dependent on economic factors and the
required effluent conditions.

2.5.1 Cadmium Precipitation

The most common treatment for cadmium and other
heavy metals is hydroxide precipitation in which lime or
caustic is added to adjust the wastewater to alkaline pH,
followed by precipitate formation, settling, and perhaps sand
filtration. Most effective precipitation for cadmium occurs
between pH 9.5 and 12.5. Freshly cadmium hydroxide has been
reported to leave approximately 1 mg/l of residual cadmium
ion in solution at pH 8 and reduced to 0.1 mg/l at pH 10
(Jenkins et.al., 1964). Bhatia et.al. (1979) reported
cadmium residual concentration of 0.014 mg/l at pH 11.5.
Co-precipitation with iron and aluminium hydroxides have
shown to give very good removal even at pH 8.5. Filtration
process reduces the effluent concentration further. Removal
of about 100 percent can be achieved throughout the pH range
from 8.7 to 11.3 by lime and excess lime treatment. Sorg
et.al. (1978) achieved 100 percent removal with a cadmium
concentration as high as 10 mg/l at pH 11.3.

Hydroxide treatment system has several problems which
include poor filtrability because of the gelatinous nature
of the hydroxide sludge, large volumes of sludge (including
gypsum if the waste is high in sulfate and lime is used for
neutralisation) and in the case of cadmium optimum hydroxide

precipitation at pH 10.4 (Patterson, 1975). Subsequent pH readjustment is needed for treatment at high pH, which increases the treatment costs and effluent dissolved solids. Most metal bearing waste streams now contain complexing agents which have been used in conjunction with the heavy metal pollutants and which in learge measure stabilize the pollutant ions against hydroxide precipitation.

Conventional coagulant treatment with alum or ferric chloride is also effective in removing cadmium from water (Culp and Culp, 1974; Sorg et.al., 1978). Iron coagulant is slightly more effective than alum, removing cadmium greater than 90 percent at pH 0.8 and above. At low alkalinity, cadmium removal by alum is dependent on turbidity. Higher turbidity gives more percentage of cadmium removal (Sorg et. al., 1978).

Carbonate precipitation treatment occurs at pH values less than those for optimum hydroxide treatment; cadmium carbonate precipitate is reported to be more dense than hydroxide precipitate, yielding improved solids separation and decreased sludge volume, and carbonate sludges are reported to have better filtration characteristics than hydroxide sludges. The pH range from 8.4 to 10.8 has been reported to give treatment of 0.25 to 1.7 mg/l cadmium. The advantage in precipitating cadmium with carbonate is that at pH 8.4, the residual cadmium concentration obtained is 1.2 mg/l while for the cadmium hydroxide system at pH 8.6, the maximum soluble concentration is 126 mg/l (Patterson et.al., 1977).

Soluble sulphides such as sodium sulphide have been used in the past to precipitate metal ions from solutions. With proper controls, such separations are generally substantially quantitatively complete, however, prior at sulfide precipitation processes have certain disadvantages which have prevented their widespread adoption. The most serious problem has been the formation of noxious quantities of hydrogen sulfide.

2.5.2 Kastone Process

The Kastone process was developed by the Du Pont Company and is recommended for the treatment of cadmium cynide. The solution pH is adjusted to 10.0-11.5, the solution is heated to 120°-130°F, and hydrogen peroxide and formalin are added according to recommendation of the supplier, depending on a previous analysis. In approximately 60 minutes, the treatment is completed. The filterability of the metal solids is improved by the process, but there is greater danger for entrapment of the insoluble metal cynides in the sludge. The chemical costs are somewhat higher with this process. The effluent requires biological treatment, so it must be discharged to a sanitary facility.

2.5.3 Ion Exchange

Ion exchange is a system for removing one ion from solution and substituting it with another ion to produce a solution that has a more desirable composition than the one being treated. Standard cation exchange resins have good selectivity for cadmium with only calcium, lead

and barium being more preferred. This treatment is utilised in plating industry for removing cadmium from rinse water enabling re-use of the water. Ion exchange resins with high specificity for cadmium are commercially available. Ion exchange can be used as a polishing treatment or a recovery process. Cadmium removal by ion exchange may be pH dependent (Sorg et.al., 1978). Linstedt et.al. (1971) removed 99 percent cadmium by a cation exchange process and 99.9 percent by cation and anion exchange. In ion exchange process sludge handling can be expensive since cadmium separation can be a complex. Large installations are required to provide the exchange capacity needed between regeneration cycles (Patterson and Minear, 1973) because of the limited capacity of ion exchange system. Design considerations have to be very carefully weighed.

2.5.4 Reverse Osmosis

Reverse osmosis separates pure water from its contaminants rather than removing contaminants from the water. Cadmium removal has been worked with prepared thin films of cellulose acetate semi-permeable membranes, which can operate between a pH range of 4-8. Toxic metals from metal plating industrial wastes have been treated successfully by reverse osmosis. However, Hindin et.al. (1968) obtained 70 percent removal of cadmium at different initial concentrations conducting laboratory tests employing reverse osmosis. If removal is limited to 70 percent only, this technique would be useful only for initial cadmium levels of

very low concentrations. It is a costly process and the
influent of the system does have certain restrictions like
dissolved solids concentration (2 to 5%), its narrow accep-
table temperature range for satisfactory operation (35-85°F),
concentration of iron and manganese (allowable below 0.3 ppm),
free chlorine (allowable below 0.2 ppm). Suspended solids
must be less than 10 μm in diameter.

2.5.5 Foam Fractionation

Foam fractionation (separation) can be applied
for removal of heavy metal ions by using an anionic surfactant.
Foam fractionation is defined as the particle separation of
dissolved (or sometimes colloidal) substances from liquid by
adsorption on the surface of bubbles which ascend through the
liquid to form a foam which then retains the adsorbed subs-
tances (Lemelich, 1972). Chou and Okamato investigated the
removal of cadmium from aqueous solution by foam separation
using chelating agents under various conditions. They found
that cadmium can be successfully removed by foam separation
using sodium dodecyl benzene sulphonate or 4-dodecyl diethy-
lene triamine surfactants.

2.5.6 Adsorption Techniques

Interest has risen recently in removing cadmium
ions from solution using adsorption techniques. Many inves-
tigations on the sorption of cadmium on activated carbon
(Linstedt et.al., 1971; Netzar and Norman, 1973; Huang and
Ostovic, 1978; Huang, 1980; Huang and Smith, 1981; Huang
and Wirth, 1982), starch xanthate (Wing et.al., 1975),

discarded automotive tires (Netzer, 1974), serpentine mineral (Sunderesan et.al., 1978), Giridih bituminous coal and activated rice husk (Bhattacharya, 1983) have been conducted.

To materialize widespread use of adsorption process, there is a need to furnish adsorbents designed to offer a low-cost treatment options. Efforts have been made in removing cadmium and other metal ions from solution by binding with such agricultural materials such as waste wool, nut wastes, tree barks and modified cotton (Masri and Friedman, 1974, Randall et. al., 1974). The obvious advantage of such adsorbents compared to other processes such as ion exchange, by resin, reverse osmosis and adsorption on activated carbon, is their lower cost (Larsen and Schierup, 1979).

Natural byproducts such as chitosan (produced by deacytylation of chitin) (Masri et. al., 1974; Muzzareli and Rocchetti, 1974; Nair and Madhavan, 1982) and miloganite (Masri et.al., 1974) have shown promise in binding heavy metal ions. Chitin [(1 $\rightarrow$ 4) - linked 2 acetamido-2-deoxy-β-D-glucan] and its N-deacytylated derivative, chitosan, display specific binding characteristics. Chitin adsorbs wheat germ agglutinin, phosphorylases and a specific protein present in crab shell. Chitosan adsorbs Ti^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Cd^{2+}, Zn^{2+} and Hg^{2+}, but not Li^+, Na^+, Mg^{2+}, Si^{2+}, K^+ and Ca^{2+}. The adsorption of uranium on chitin, chitosan and their phosphorylated derivatives has also been reported and a structure was proposed for the uranyl chitosan complex.

2.6 Chemistry of Chitin and Chitosan

2.6.1 Sources and Characteristics of Chitin

Chitin occurs widely in lower animals, fungi and crustacea. The exoskeletons of prawns (Penaeus indicus), crabs (Scylla serrata), and lobsters, rich in chitin which are thrown out as waste from processing plants in large quantities, have attracted the attention of the scientists and technologists as a raw material for chitin production, all over the world during recent years. The prawn processing industry in India turns out over 60,000 tonnes of waste comprising head and shell containing about five percent chitin. Consequent on the demand of squid (Loligo sp.), the squid fishery is also gaining in importance lately. The squid pen provides pure chitin in large amounts. Squilla (Oratosquilla nepa), constitutes another important source for chitin, a considerable portion of the trawler catch along with prawns in certain seasons. In India, Squilla is not at all used for human consumption as it does not contain much meat and hence the catch is thrown back into the sea itself (Nair and Madhavan, 1982). Exoskeletons contain from 20 to 50 percent chitin (Vaidya and Bulusu, 1984).

As more and more uses are discovered for chitin, chitosan and their derivatives in recent years, research efforts have intensified in identifying microorganisms capable of degrading and producing these compounds. Warnes and Rux (1982) examined the mineralization rate of particulate chitin in a small fresh water lake in east central

Indiana. They found that the sediment-water interface is the most active site of chitin mineralization in the lake environment. The chitin content of sediments depends not only on the initial chitin content of skeletal components but rather on the way those skeletal structures withstand weathering. Despite their fundamental interest in basic ecology, there are very few if any quantitative data on chitin biomass in natural environment.

The production of chitin is connected very closely with that of the fishing industry and has been increased constantly within the recent years. In U.S.A. and Japan chitin and chitosan are produced these days in an industrial range. The raw material is supplied by the crab fishing industry (Gross et.al., 1982).

Chitin is a polysaccharide polymer containing 2-deoxy-2 amino glucose units linked through $\beta-1,4$ linkages. It is hydrophilic, inert, and nonbiodegradable. It has been reported that every five amino groups out of six in the chitin molecule are in the acetylated form.

The most acceptable structure of most abundant α-chitin was proposed by Carlstrom (1952). The fiber repeat is identical with that of cellulose and the unit cell contains two antiparallel chains. There are two types of hydrogen bondings involved; an intramolecular O-3'...O-5 hydrogen bond and an intermolecular NH...O=C hydrogen bond between the amide groups which lies almost perpendicular to the fiber axis. Figure 2.4 shows the primary structure of chitin

with three repeating units (Labischinski and Naumann, 1982).
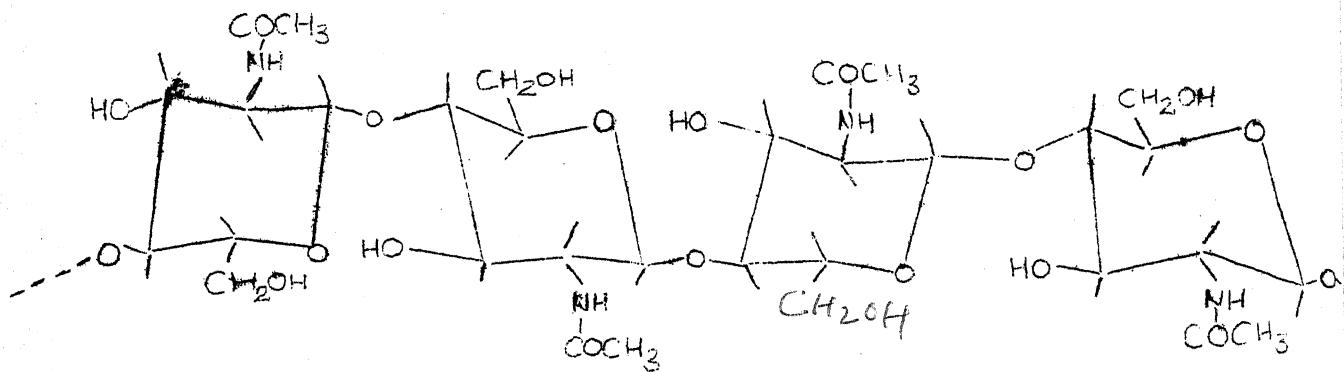
Figure 2.4   Primary Structure of Chitin.

The insolubility of chitin is suggested to be due to the rigid crystalline structure supported by the inter- and intramolecular hydrogen bonds. Chitin is closely associated with protein, inorganic salts such as calcium carbonate, and lipids including pigments. To remove these substances successfully, following procedures are usually employed. Decalcination by immersing in a diluted hydrochloric acid or in an EDTA solution; deproteinization by heating in aqueous alkali, and removal of lipids by extracting with hot ethanol.

The dry, flake like chitin contains not more than 5% moisture and usually upto 3% ash. Colour varies from creamy white to light-pink or light-yellow tan. Acetyl contents of α, β and γ -chitin are 7.3%, 9.31% and 11.10% respectively.

2.6.2 Chitosan and Its Characteristics

Chitosan is generally prepared from chitin by N-deacetylation with alkali and now commercially available

in a ton scale. Chitosan or deacetylated chitin in acidic

medium develops a violet or reddish colour with iodine.

Chitosan, the dry, flake-like substance, contains not more

than 5% moisture and has a white or white-pinky colour.

While chitin is insoluble in most solvents, chitosan is

readily soluble in acidic solutions and more available for

industrial applications. Chitosan is insoluble in water, in

organic solvents and in alkali. In the presence of a limited

amount of acid it is soluble in water-methanol, water-

ethanol, water acetone and other mixtures.

Chitosan is soluble in formic and acetic acids. Even

though a systematic survey was not reported, other organic

acids fail to dissolve chitosan. Inorganic acids can diss-

olve chitosan at certain pH values after prolong stirring

and heating. Nitric acid can dissolve some chitosan but

sometimes after dissolution one can observe a jelly white

precipitate. Hydrochloric acid also requires heating and

stirring for hours. Sulphuric acid does not dissolve chito-

san.It forms chitosan sulphate. At a concentration of 2 x

10^{-5} M chitosan completely inhibits the fermentation of

glucose by a 0.03% yeast suspension (Ralston et.al., 1964).

At the said concentration it caused an aggregation of yeast

cells which can be observed under microscope. At higher

concentration of 2 x 10^{-3} M the yeast was not aggregated,

(Vaidya and Bulusu, 1984).

Effective deacetylation of chitosan is readily attained

by intermittently washing the intermediate product in water

two or more times during the alkali treatment. The molecular weight of chitosan obtained by Mima et.al. (1982) was 5×10^5 at the most deacetylation of nearly 100%.

According to Wu and Bough (1978), deacetylation proceeds to about 70% within the first one hour of alkali treatment in 50% NaOH solution at 100°C but it progresses only gradually after this, reaching 80% in five hours. Further alkali treatment does not deacetylate significantly and only degrades the molecular chain. Reaction temperature has significant effect on the deacetylation rate. The rate at 110°C is more than twice as rapid as at 60°C. High reaction temperature, however, has the effect of decreasing the molecular weight. Figure 2.5 shows whole process of deacetylation.

```
        ┌─────────────────────┐
        │    Chitin Source    │
        └─────────────────────┘
                   │

        Alkali Treatment by NaOH
          ( 40-50%) in N₂
                   │

        Washing in Distilled Water
                   │
        ┌─────────────────────┐
        │      Chitosan       │
        └─────────────────────┘
```
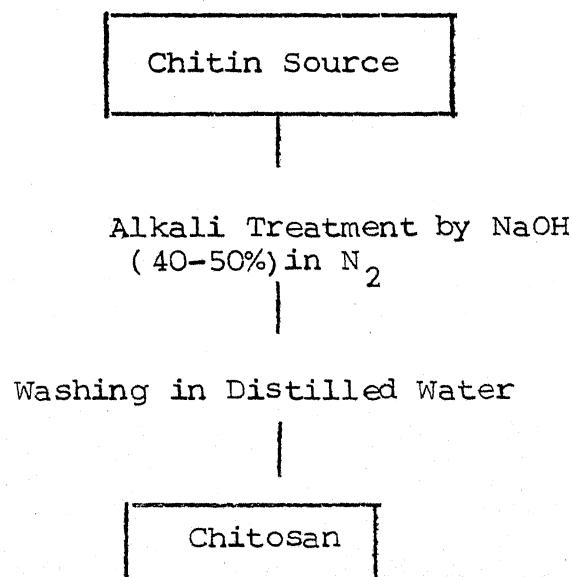
Figure 2.5   Whole Process of Deacetylation.

Tensile strengths of chitosan in the dry state range from 610 to 1050 Kg/cm^2. The mechanical strengths tend to increase if the sample has a larger molecular weight and/or is more deacetylated. The acetyl content of chitosan can be determined by infrared spectroscopic method.

Chitosan is dispersible in aqueous solution under acidic conditions by virtue of its polycationic nature. The structure of the chitosan repeat unit is shown in Figure 2.6 along with structures of some common functional polysaccharides. It can be seen that the structure of chitosan is similar to that of other polysaccharides. Chitosan is depolymerized by halogenolysis accompanying deaminition and oxidation reactions via chitosan-halogen complexes. A colour reaction of chitosan with iodine has been used for the detection of chitosan and partially N-deacetylated derivatives of chitin.

2.6.3 Uses of Chitin and Chitosan

Chitosan, a naturally occurring polymer has not yet been considered as potential raw material sources for industrial purposes because of its low processibility, and also because of lack of higher functionality. Recently utilization of chitin and chitin derivatives have been attempted. Micro crystalline chitin, a partially degraded low molecular weight chitin, has apparent potential in both medical and nutrition applications (Deschamps and Castle, 1982).

The application of chitosan to pulp and paper industry has long been studied by several groups of workers. Chitosan

32
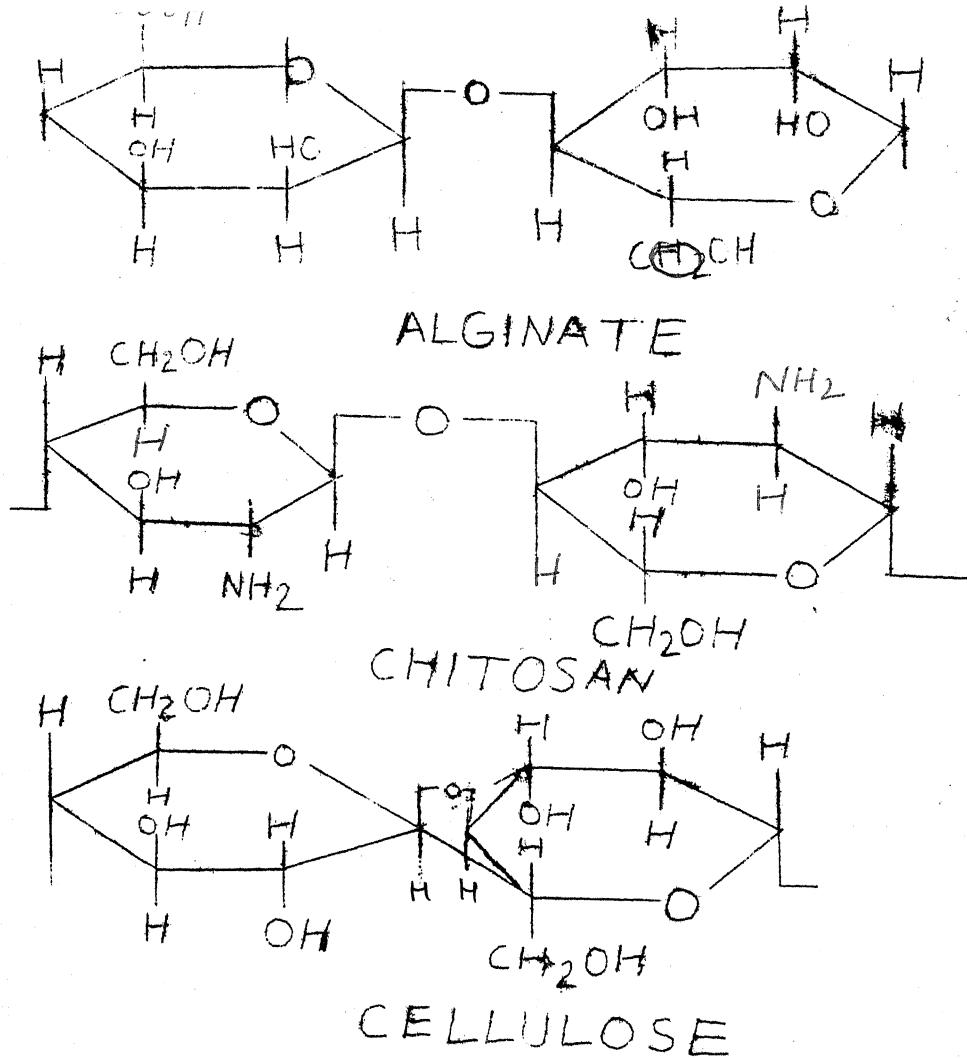
Figure 2.6 **S**tructure of Chitosan and Other Polysaccharides.

coating was found to contribute to increase of surface strength of machine-made Japanese paper. Regenerated chitin fiber paper with considerable strength was made when used N-substituted chitin fibers as biders. In paper industry it is hoped that cationic fibers like chitin and its derivatives are effective in acceleration of drainage, increasing retention of fines and fillers as well as sizing effect. The development of chitin fiber paper is also long awaited from the viewpoint of medical utilization (Kobayashi et.al., 1982). Nutritional studies have shown that a combination of chitinous products and whey in isonitrogenous isocaloric

diets enabled broiler chickens to utilise whey more efficiently. Several new uses of chitin have been demonstrated in recent years including medical sutures, film and fiber products, and derivative compounds (Brine and Austin, 1975).

It has been demonstrated that as little as a 1% chitinous amendment to potting mixture can cause a significant increase in the population of chitinolytic actinomycetes. This treatment also causes a reduction in root-knot infestation in plants (Lewis and Susan, 1982).

Both chitin and chitosan are capable of displaying significant host defence effect in animals challenged with tumor cells and pathogenic microbes (Suzuki et.al., 1982). Chitosan can be a useful ingredient in hair cosmetic products, without the disadvantages of the synthetic polymers, used generally for the same purpose (Wella et.al., 1982). Chitosan also finds application in foods, textile finishing and printing, chromatography etc. Chitosan improves the functional properties of fish packaging materials.

2.6.4 Chitosan Application in Water and Wastewater Treatment

A partially deacetylated chitin (a chitosan with less than 7% nitrogen content) may be used in treating turbid matters in an aqueous solution (Peniston and Johnson, 1977). Chitosan has been evaluated as an effective coagulating agent. Bough et.al. (1975) have reported that the effect of chitosan on coagulation of suspended solids in various food-processing wastes such as poultry, egg, vegetable, cheese whey, sea food wastes and activated sludge, and these

byproducts have no adverse effect upon animals at chitosan levels below 5% of the diet. However, it is required to disinfect microorganisms when byproducts from waste is used for feeds.

Wu and Bough (1978) studied chitosans with varying chemical characteristics and molecular weight distribution for their effectiveness as waste treatment agents for conditioning of activated sludge and cheese whey. Parasan 27 marketed in India has been reported to be modified chitin by the producers with good clarification properties. At the Central Institute of Fisheries Technology in Cochin (Prabhu et.al., 1976) muddy water which was prepared by suspending finely ground brick powder in ordinary water, was inoculated with chitosan and alum in doses of 10 mg/l. In samples studied after 45 minutes, the bacterial load has been reduced much more by chitosan than alum.

Vaidya and Bulusu (1984) have reported that chitosan is a potential coagulant and coagulant aid for the removal of turbidity from water and is capable of working even low turbidity waters. The reduction in turbidity was found remarkable at high turbidities even at comparatively low doses. Emulsions with an emulsified oil concentration in the range of 1000 to 4000 ppm and stabilized by anionic surfactants can be efficiently flocculated by addition of chitosan (Axberg et.al., 1980). The application of chitosan did not significantly change the pH of the treated water and did not contribute to the organic content of treated

water. By preliminary cost analysis, Vaidya and Bulusu
(1984), showed that considerable savings are possible when
chitosan is applied in water treatment as coagulant or
coagulant aid.

The presence of amino groups in the chitin molecule
provides a binding site for proteins. The capacity of chito-
san conditioned in ammonium sulphate and/or sulfuric acid
for collection of metal ions has been discussed by Muzzarelli
et.al. (1974). They also reported that the difference in pH
of the solution influence the metal ion adsorption capacity of
chitosan. The adsorption characteristics of chitosan prep-
ared from four different sources, namely, crab, prawn squid
and squilla in the case of Fe^{3+}, Co^{2+}, Ni^{2+}, Hg^{2+} and Cu^{2+}
ions were studied by Nair and Madhavan (1982). The behaviour
of chitosan from these four sources did not differ markedly.
In all cases quantity of different metal adsorbed varied
considerably irrespective of the source of chitin.

Madhavan and Nair (1978) found that viscosity and
adsorption capacity of chitosan are independent of each other.
Separation of trace elements from sea water by chromatography
on chitosan was reported (Muzzarelli et.al., 1970). Accor-
ding to Masri et.al. (1974), the greater effectiveness of
chitosan for metal binding may be due in part to the greater
basicity of the aliphatic primary amino group (pK about 10).
Tney showed the potential utility of chitosan for removing
and concentrating heavy metals from industrial effluents and
other water sources. Muzzarelli et.al. (1970) proposed

chitosan as a chelating chromatographic support suitable for pollution detection survey and abatement, for wastewater purification and recovery of trace metal ions for analytical purposes. The adsorption of uranium by chitin (Tsezos and Volesky, 1982; Tsezos, 1983) and by chitin phosphate and chitosan phosphate has been found. Kume and Takehisa (1982) reported the γ-irradiation on disinfection and recovery of protein from wastewater with chitosan. Irradiation can improve the coagulating properties of chitosan.

2.7 Surface Charge Characteristics of Sorbent

Parks (1967) showed that if the surface area is large, the development of the electrical double layer may lead to important changes in the solution composition and pH. Because, the behaviour of suspension is determined or modified to a great extent by the charge associated with the solid phase, Parks (1967) introduced the concept of zero point of charge, zpc, or isoelectric point of the solid, IEP(s), both terms mainly related to pH. The pH, at which the solid surface charge from all sources is zero, is called the zero point of charge (pH_{zpc}). pH_{zpc} can be distinguished by pH at zero net adsorption of protons and hydroxide ions, i.e., $\Gamma_{H^+} - \Gamma_{OH^-} = 0$. From this argument, ideally, pH_{zpc} will be independent of the electrolyte concentration (Huang, 1981).

The zero point of charge values give indications on the behaviour of various sorbents in the aquatic environment. Below pH_{zpc} the surface is positively charged and it behaves as a cation exchanger, whereas, above pH_{zpc} the surface is

negatively charged and behaves as anion exchanger. Maximum coagulation and sedimentation rates occur at zero point of charge. Anion and cation adsorption capacities are equal and minimum at zero point of charge (Parks, 1981).

2.8 Summary

From the literature review it is apparent that cadmium is probably the most harmful and insidious pollutant because of its non-biodegradable nature and its potential to cause adverse affects in human beings at certain level of exposure and absorption. Because of its toxicity, cadmium is not suitable for waterborne discharge. The specified discharge limit is often below 1 mg/l. Despite its potential toxicity it is widely used and particular industries rely on solutions of the cadmium ions.

Wastewater from electroplating plants, spillage through galvanization effluents besides the runoff from agricultural lands infested with phosphatic-fertilizer and pesticides are the primary source of cadmium pollution.

The treatment options available for cadmium removal have been reviewed. Interpreting the data available on various treatment options, it has been observed that adsorption process offer most potential cadmium removal mechanisms. Adsorption of cadmium on activated carbon appears to be an attractive method. Chitosan has recently been proposed as an excellent adsorbent for heavy metals. There is a need to undertake an investigation of this natural polymer for removing cadmium pollution.

3. SCOPE OF THE WORK

In the present study, an attempt is made to evaluate the adsorptive capacity of chitosan which is a natural polymer. Chitosan is N-deacetylated derivative of chitin structural polysaccharide and is a waste product from prawn, crab and shrimp canning industries. The ability of chitosan to complex metal ions has been reported in literature. The present work is carried out along the following lines.

(1) Batch sorption tests to evaluate the important sorption parameters.

(2) Experiments determining the rate limiting step in sorption of cadmium on chitosan.

(3) Effect of chitosan/cadmium ratio, pH, temperature, calcium concentration and various sizes of chitosan on sorption kinetics of cadmium.

(4) Equilibrium studies to compare the cadmium sorptive capacities of various sizes of the sorbent.

(5) Effect of competitive ions, EDTA and ionic strength on sorption of cadmium.

(6) Batch tests for desorption of cadmium from the cadmium loaded chitosan.

(7) Regeneration studies for chitosan.

(8) Downflow column studies to remove cadmium from water using a laboratory column.

4. MATERIALS AND METHODS

4.1 Glassware

All glassware used in the present study was of 'pyrex' quality manufactured by Borosil Glass Works Ltd., Bombay and marketed under the brand name 'Corning'. All glassware were washed with TEEPOL (manufactured by Surfactant Pvt. Ltd., Bombay) followed by tap water and distilled water. The glassware were finally soaked overnight in cadmium solution of the same concentration used in experiments. Prior to use they were rewashed with glass-distilled water. It was expected that this procedure would effectively block the active sites on the glass to eliminate any error being introduced from the sorption of cadmium on glassware in the actual experiment.

4.2 Water

Water used in all batch sorption experiments was laboratory distilled water redistilled in a glass distillation still. The average pH of this redistilled water was 6.5 and conductivity varied between 4.7×10^{-6} and 6.2×10^{-6} siemens/cm. Tap water was used to prepare the raw water feed for the column studies. The analysis of the tap water is given in the Table 4.1.

4.3 Chemicals

All chemicals used were of analytical reagent grade. Stock cadmium solution (1 g/l) was prepared from cadmium nitrate and this was used to prepare working solutions for daily experimental work.

Table 4.1

Analysis of Tap Water

1.	pH	7.8 - 8.0
2.	Turbidity	Not detectable
3.	Conductivity	1.26×10^{-3} Siemens/cm
4.	Alkalinity	367 mg/l as $CaCO_3$
5.	Hardness	162 mg/l as $CaCO_3$
6.	Calcium hardness	82 mg/l as $CaCO_3$
7.	Chloride	37 mg/l as Cl^-
8.	Cadmium	Not detectable

4.4 Sorbent

The sorbent used was chitosan. Chitosan was prepared in the laboratory by N-deacetylation of chitin in alkali solution. Chitin was obtained from Chempure Ltd., Calcutta.

4.4.1 Preparation of Chitosan

The chitin was treated for five hours in 50% NaOH solution at about 80°C under nitrogen atmosphere. Chitosan, the hydrolysis product obtained by the alkali treatmeant was washed in distilled water at about 80°C to neutrality. Chitosan was dried very carefully at a temperature not exceeding 80°C. It was pulverised and sieved to a geometric mean size of 190 μm and stored in air tight glass bottle for use in sorption experiments. Other particle sizes such as 37 μm, 144 μm, 256 μm and 328 μm were also used for sorption kinetics and sorption equilibria experiment. 378 μm size chitosan was used for down flow column studies.

4.5 Analysis of Cadmium

Cadmium concentrations in the sample were estimated using IL 75/AA/AE Spectrophotometer (manufactured by Instrumentation Laboratory, Inc., Wilmington, MA 01887, U.S.A.). The operating characteristics of the instrument for the estimation of cadmium are as follows:

Light source	:	Hollow cathode
Lamp current	:	3 mA
Wavelength	:	228.8 nm
Slit width	:	320 μm
Burner head	:	Single slot
Flame description	:	Air-acetylene, oxidising flame lean blue
Sensitivity	:	The sensitivity (at 0.0044 absorbance = 1 percent absorption) is about 0.01 μg/ml for the instrument parameters described above.
Linear range	:	The working range for cadmium is linear upto a concentration of approximately 2 μg/ml (when using an aqueous solution and the instrument parameters listed above)
Interferences	:	No major interferences have been observed in air-acetylene flame.

The sample was directly aspirated which was subsequently atomized in air-acetylene flame and the intensity of the flame was measured using a Hollow cathode lamp at suitable wavelength. The anode usually employed is of tungsten. The amount of light absorbed is proportional to the amount of element present in the sample.

The instrument was initially calibrated for known concentrations and then the unknown concentration of the sample was determined.

4.6 pH_{zpc} of Sorbent

A procedure outlined by Huang and Ostovic (1978) was employed to estimate the pH of the zero point of charge (pH_{zpc}) of chitosan. It was done by fast acidimetric-alkalimetric titration method. To four identical portions of 100 ml solution containing known amounts of sodium chloride (10^{-1} M, 10^{-2} M, 10^{-3} M), 1 g of chitosan was added. The samples were agitated for 20 hours at low speed. Two samples (with chitosan) were titrated directly with acid (0.1 M HCl) and base (0.1 M NaOH). The pH values were taken at 30 sec after each aliquot of titrant was added. The other two samples were filtered and the filtrates (without sorbent) were titrated as earlier. The net titration curve for each ionic strength was obtained by subtracting the titration curve of the filtrate (without sorbent) from that of the sample (with sorbent). In the absence of specific chemical interaction between the single electrolyte and the surface, the net titration curves usually meet at a point that is defined as the pH_{zpc} (Huang and Ostovic, 1978). Figure 4.1 shows the typical titration curve for chitosan. The pH_{zpc} of chitosan was found to be 8.56.

4.7 Experimental Techniques

4.7.1 Batch Sorption Kinetic Tests

Batch sorption experiments were conducted at
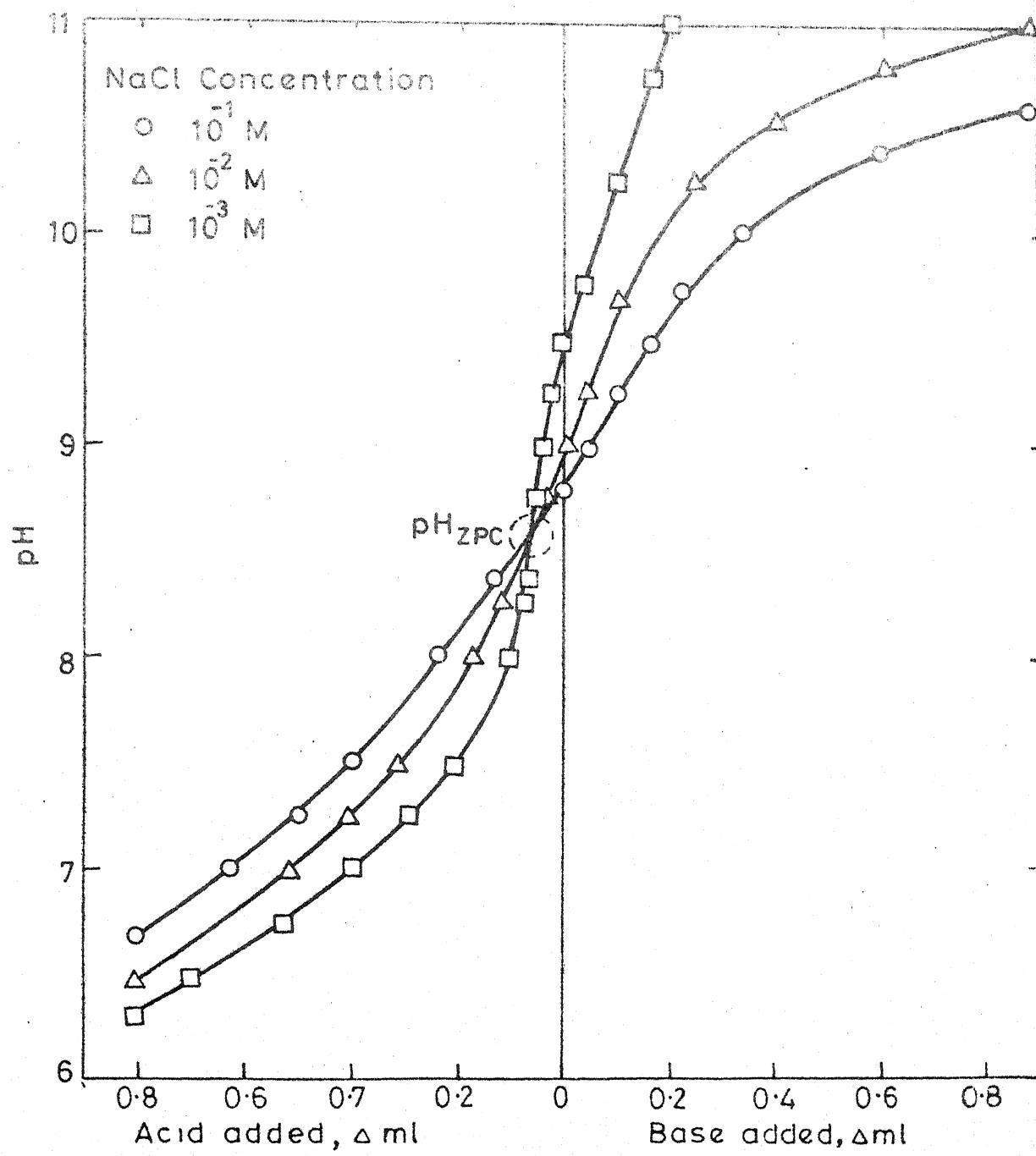
Fig. 4·1 Titration Curves for Chitosan in the presence of NaCl at Various Concentrations

20 rpm was maintained. The sorption rate study was conducted over a series of 300 ml bottles. Predetermined amounts of sorbent and sorbate were added to 200 ml sample volume. Bottles were removed at required intervals and stored in a glass test-tube for analysis of residual adsorbate. Temperature and pH measurements were taken initially and at the end of each experiment. In sorption kinetic studies initial cadmium concentration was varied in the range of 1 mg/l to 10 mg/l. The same procedure was employed to investigate the effect of pH, Ch/Cd ratio, geometric mean sizes of particles, calcium concentration, temperature and speed on the kinetics of cadmium adsorption.

Effect of temperature on the rate of sorption was conducted at two different prevailing ambient temperatures as the facility to undertake this investigation over wide range of temperatures was not available.

4.7.2 Sorption Equilibrium Studies

Adsorption isotherm experiments were conducted using the time required to attain equilibria (24 hrs) from the kinetic studies. The adsorption isotherm consisted of mixing a known amount of chitosan with several concentrations of cadmium solution in the sample bottles. 500 mg/l of chitosan was used in these studies.

4.7.3 Effect of pH, Chloride Concentration, Ionic Strength, EDTA, and Zinc Concentration on Sorption

The effect of pH at various reaction time on cadmium sorption was studied. The pH was adjusted in the range of 3 to 10 using either 0.1 N HCl or 0.1 N NaOH.

Effect of chloride, ionic strength and EDTA on cadmium sorption was studied by adding different concentrations of these substances in 5 mg/l of cadmium solution. Effect of zinc concentration on cadmium sorption was studied by varying concentrations of zinc and cadmium both.

4.7.4 Batch Desorption and Regeneration Studies

Following a two-hour adsorption period, the cadmium laden chitosan was separated from solution and immersed in distilled water adjusted to same pH.

For desorption kinetic studies initially 3 gm of chitosan was loaded with cadmium using 200 ml of 100 mg/l cadmium solution and a contact time of 24 hours. Experimental conditions were similar to that of batch sorption tests. The amount of cadmium sorbed was determined by measuring the concentration of cadmium remaining in solution. The cadmium-laden chitosan was then filtered and washed gently with double distilled water to remove any unsorbed cadmium in the film of liquid adhering to chitosan. This was followed by air drying. Cadmium was then allowed to desorb by suspending 500 mg/l of Cd-saturated chitosan in (a) 200 ml of double distilled water and (b) 0.01 N HCl with agitation. Same as sorption kinetic experiments, several bottles were used and the bottles were removed from the shaker at desired time intervals and supernatant analysed for cadmium.

For sorbent regeneration studies, the same procedure as above was employed for cadmium loading. 200 mg of air-dried cadmium-saturated chitosan was suspended in 200 ml of

regenerant solution (0.01 N HCl) with agitation for 12 hours following which cadmium sorbed was determined. Chitosan was then filtered, washed and air-dried before subjecting to next loading cycle. The loading-regeneration cycle was repeated three times.

4.7.5 Column Studies

Glass column with 1.0 cm inside diameter was filled to a depth of 30 cm. Chitosan particles (geometric mean size 378 μm) was used. Glasswool was placed at the bottom of the column to hold the chitosan. The influent cadmium solution was stored in a 10 litre bottle. The column was operated in a downflow packed bed mode. Turbidity-free tap water containing 5 mg/l cadmium at lowered pH 6.9 was fed to the column without any treatment. A constant flow rate of $3 \, M^3/M^2/hr$ was maintained manually. The samples of the influents and subsequent effluents were periodically collected and analyzed for cadmium.

5. RESULTS AND DISCUSSION

Results of all experiments are presented in graphical and tabular form. In order to facilitate presentation, a discussion of the results follows each phase of the experimental work. The results of the experiments devoted to obtain an understanding of the complex nature of chitosan-cadmium sorption interactions are presented and discussed first.

5.1 Sorption Kinetics

The important physicochemical parameters which help defining the type of sorption and evaluating the process of sorption are kinetics and sorption equilibria. The study of the kinetics of the system is important from the fact that it determines the rate at which equilibrium is approached. The solute uptake rate by sorbent, obtained from kinetics of sorption, governs the contact time and this is an important characteristic defining the efficiency of sorption. Sorption equilibrium study is important in determining the feasibility and capacity of the sorbent for sorption. An efficient adsorption process has two basic requirements: (1) rapid removal of pollutants from the solution and (2) a large ultimate capacity for adsorption.

The rate at which a solute is removed from a solution depends upon the mass-transfer coefficient (rate coefficient) and upon the departure of the system from equilibrium. The uptake of cadmium by chitosan with time at pH 6.5 using

initial cadmium concentrations of 1.5 mg/l, 5 mg/l and 10 mg/l is presented in Figure 5.1. It appears that cadmium adsorption by chitosan is a rapid process. The rate of sorption was very rapid within the first fifteen minutes of reaction time and decreased markedly upto 2 to 6 hours and gradually approached equilibrium. It is evident from Figure 5.1 that equilibrium is obtained more rapidly for lower concentration of cadmium solution. The initial sorption rate which is quite high for the first 15 minutes may be termed as an instantaneous sorption.

The cadmium sorption-mechanism appears to consist of the following processes that are described below.

Amino groups of the chitosan network act initially as cadmium coordination sites. The ability of chitin and chitosan to complex metal ions has been reviewed in literature. The ability of substituted polysaccharides to retain transition metals has been correlated to the percentage of nitrogen in the polymer chain. Chitosan contains one linear amino group per glucose unit and thus exhibits much higher capacity. The amino group has an electron pair available for coordination.

Another hypothesized cadmium sorption mechanism involves the adsorption of additional cadmium by the chitosan network, close to that complexed by the chitosan-nitrogen. The experimental results provide evidence supporting the proposed adsorption process.
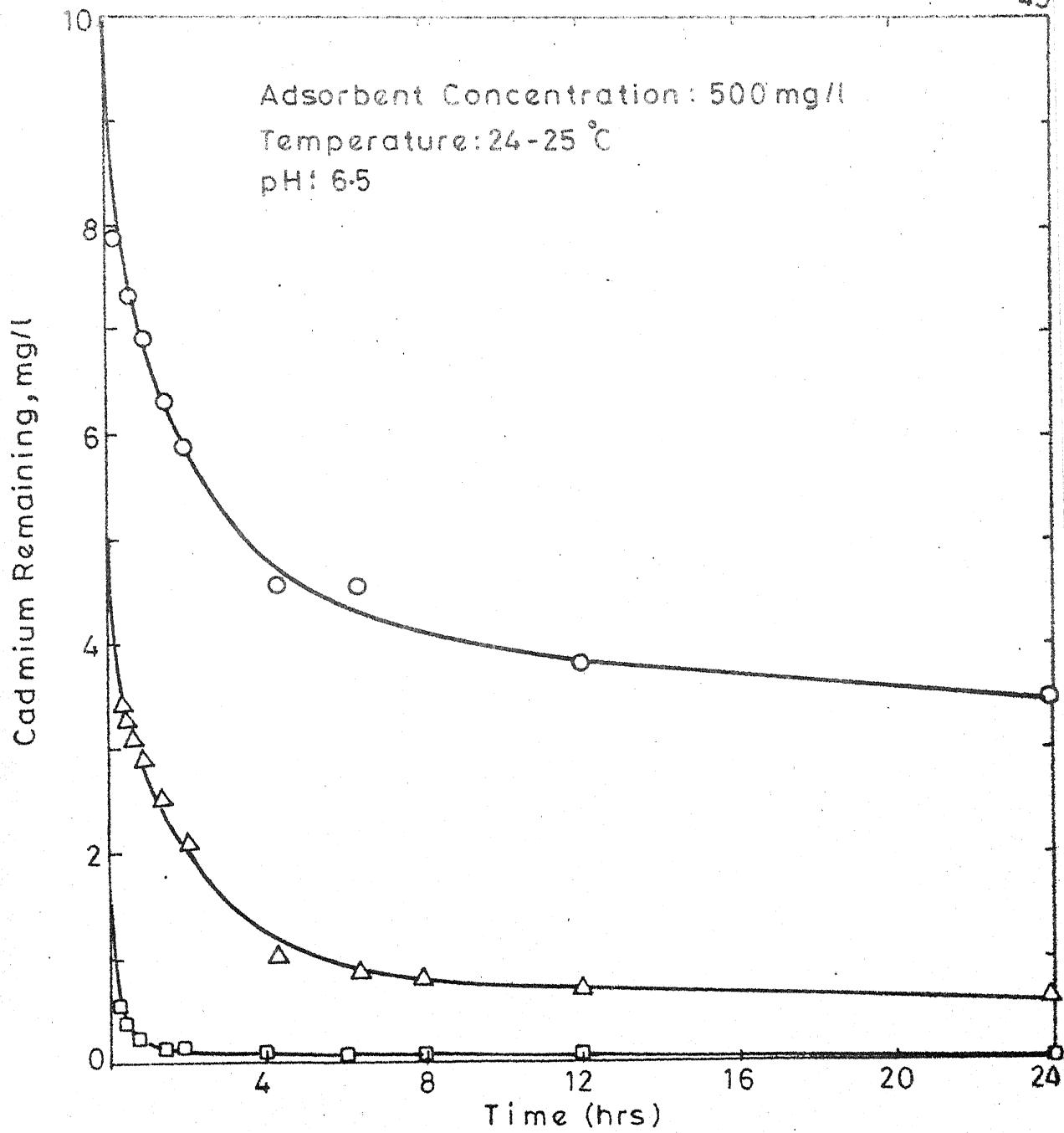
Fig. 5·1   Sorption Kinetics of Cadmium on Chitosan at Different Initial Concentrations

Adsorption is a very fast phenomenon when it is not limited by mass transfer. Chemical complexation and adsorption are both rapid processes and can, therefore, account for the observed rapid rate of adsorption initially. Complexed cadmium appears to act as a nucleation site for the further deposition of cadmium. In a recent presentation on uptake of metals by the cell wall of bacterium B. subtilis, Beveridge (1980) also suggested that chemically retained metals may act as nucleation sites for further deposition of metal in the cell wall. This was also hypothesized by Tsezos and Volesky (1982) in the case of uranium adsorption by chitin.

5.1.1 Effect of Solution pH on Adsorption

Figures 5.2 and 5.3 illustrate the effect of pH on the extent of cadmium adsorption. It was noticed that final pH values after adsorption deviated to various degrees depending on initially adjusted values. At pH 3 adsorption occurred at a slower rate attaining only 18% at equilibrium. A sudden increase in adsorption occurred by an increase of pH by one unit. This type of behaviour is specially true for hydrolysable cations (James and Healy, 1972). After pH 4 the adsorption increased linearly upto pH 9 and a little decrease occurred at pH 10.

It is clear that adsorption behaviour of cadmium metal ions is similar to metal ion in hydrolysis and is characterised by a steep pH-adsorption edge (Leckie and James, 1974). Adsorption edge is a critical pH range, often less than 1 unit wide, over which the fractional amount of metal
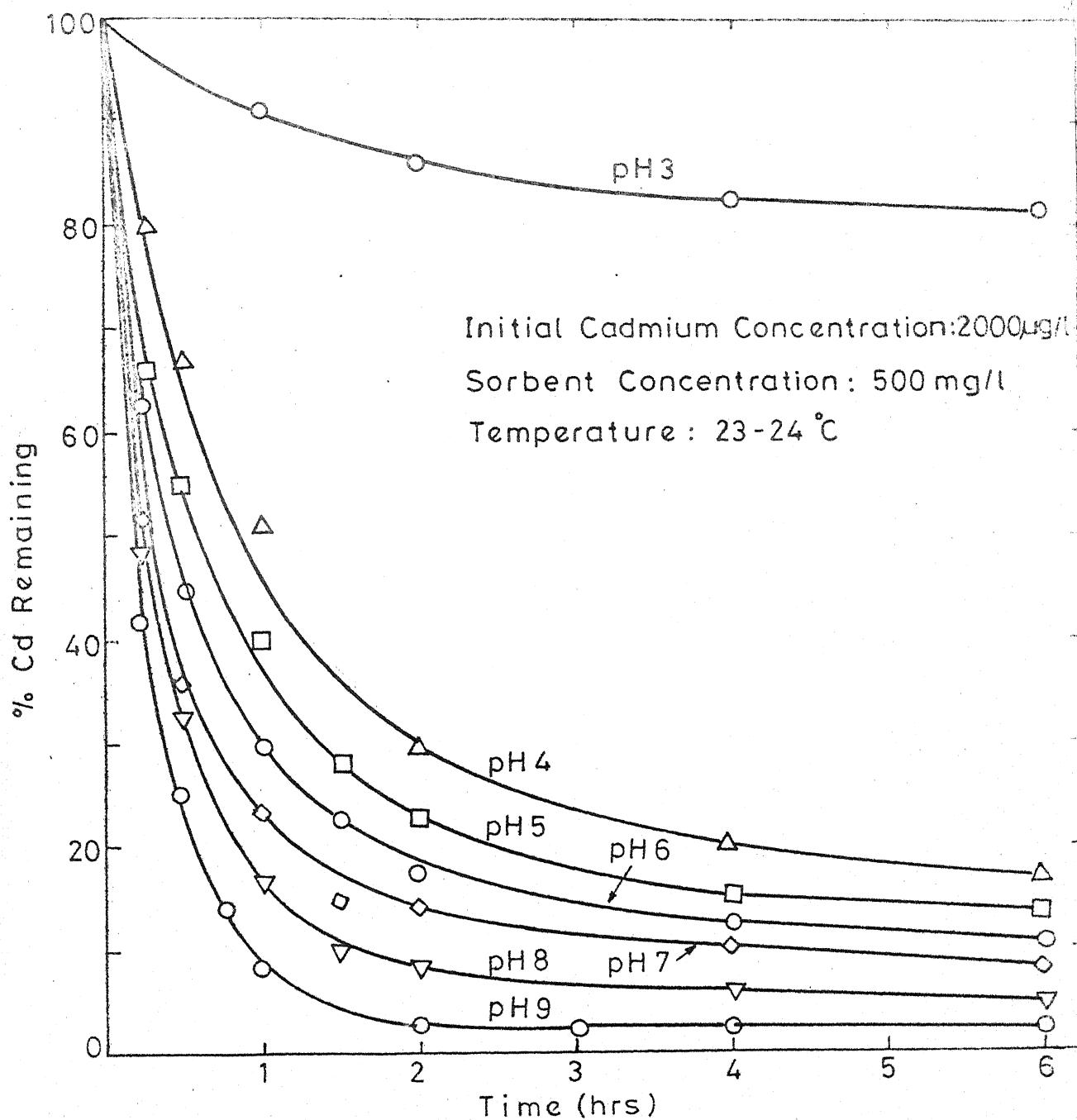
Fig.5·2   Effect of pH on the Kinetics of Cadmium
Adsorption on Chitosan

The figure shows the effect of pH on cadmium adsorption on chitosan. The y-axis is "% Cd Remaining" (0 to 100) and the x-axis is "Time (hrs)" (0 to 6). Curves are labeled pH 3, pH 4, pH 5, pH 6, pH 7, pH 8, and pH 9.

Initial Cadmium Concentration: 2000 μg/l

Sorbent Concentration: 500 mg/l

Temperature: 23-24 °C
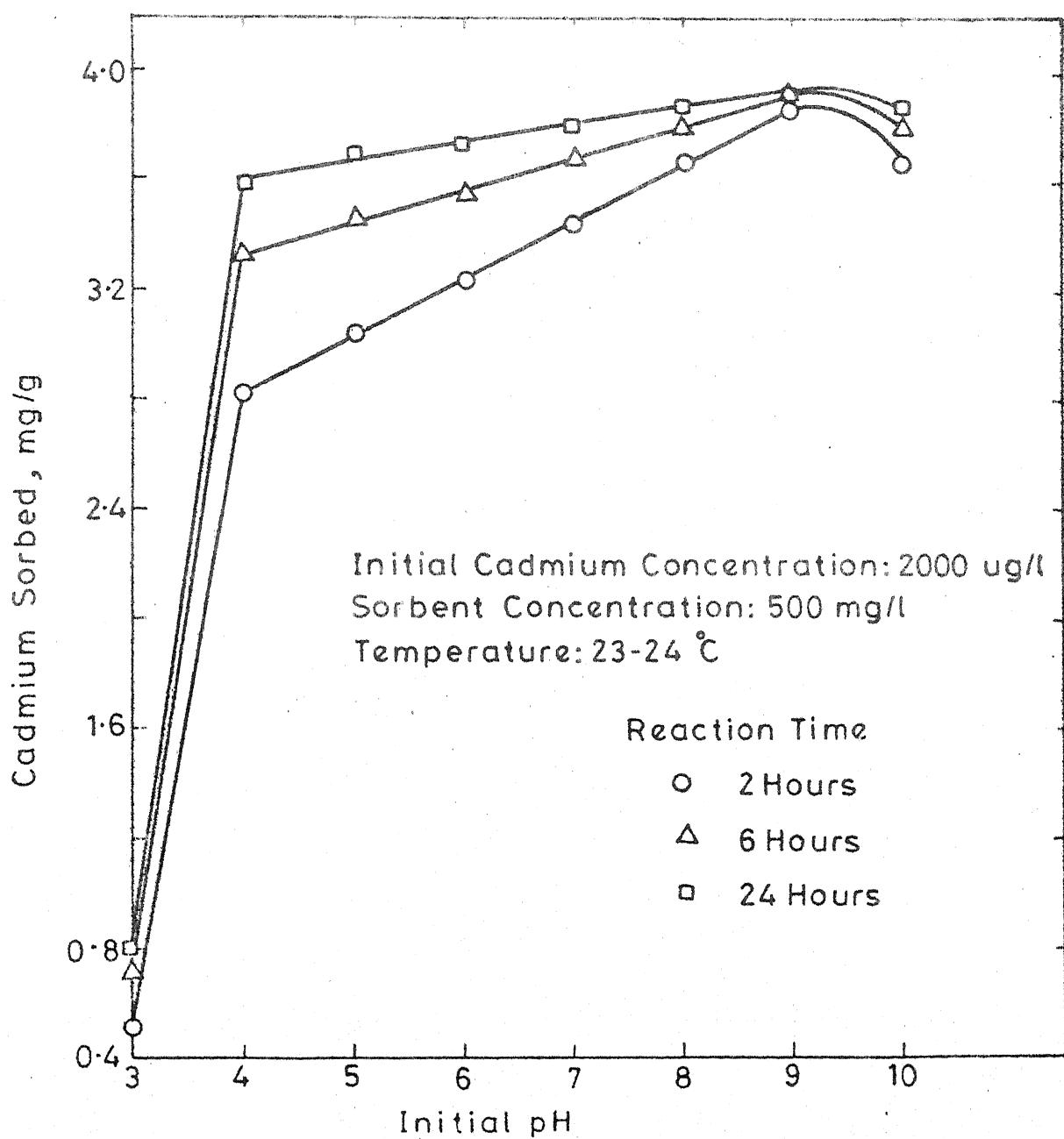
Fig.5·3   Effect of pH on Cadmium Sorption

adsorbed increases from nearly all in the solution phase to nearly all adsorbed phase, provided sufficient adsorption sites and/or adsorbent area are available.

Studies of metal adsorption in simple systems have consistently shown that pH is the dominant solution parameter controlling adsorption and the cation adsorption increases dramatically as solution pH increases (Hohl and Stumm, 1976).

There are at least three possible ways in which sorption of a metal-ligand complex may depend on pH (Benjamin and Leckie, 1981), viz., (i) sorption of the complexed metal may be chemically analogous to and have similar pH dependence as that of the uncomplexed metal, (ii) sorption of the complex may be similar to that of the free ligand, and (iii) the complex may not sorb at all. Real systems may be represented by combination of the limiting cases, and sorptive behaviour of a given complex in a given system will depend on the identity of the surface, electrolyte composition of the solution, surface electrical potential, etc. In the first two situations, the complex may sorb more or less strongly than the uncomplexed species. Thus case (iii) is a limiting case in which the complex sorbs much less strongly than either the free metal or free ligand.

Representing the chitosan monomer unit by GN, the dissociation equation of the amine could be given by

$$GN^+ : H + H_2O \;\rightleftharpoons\; GN : + H_3O^+$$
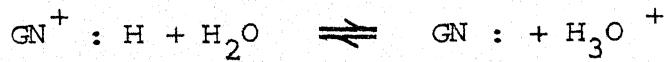
Adsorption is obviously a function of solution pH. Metal ions that would coordinate with the lone electron pair of

the amine nitrogen would have to compete with the H_3O^+ ions for the active sites. A reduced cadmium loading on chitosan is observed at lower pH values, most likely due to the increase in H_3O^+ concentration at the lower pH. Lower chitosan loadings at low solution pH have also been reported in literature by Muzarelli and Tubertini (1969) who indicated qualitatively a decline in the metal uptake capacity of chitin and chitosan for an extended series of metals, when the solution pH was reduced from 7 to 2.5. Lower chitin uranium uptake at low pH values was also observed by Tsezos and Volesky (1982) and Tsezos (1983). Masri et.al. (1974) found that one gram chitosan neutralised 5 m moles HCl within hours, also forming a gel. One gram also neutralised 5 m eq H^+ from H_2SO_4 (without gel formation, chitosan gains weight). Thus hydrogen ion may compete with other cations for binding sites of chitosan.

Cadmium forms soluble complexes with both organic and inorganic ligands in aqueous solution. Hydroxide, chloride and carbonate ligands are of particular interest to natural water and industrial wastewaters. In the case of cadmium-redistilled water system, soluble complexes of cadmium formed by combination with hydroxide are of particular interest. A cadmium hydroxide solubility curve (stability diagram), in which the total soluble metal is given by the summation of all soluble metal species and is presented in Figure 5.4 (Bhattacharya, 1983). The distribution of cadmium species is a function of pH. Based on the initial cadmium
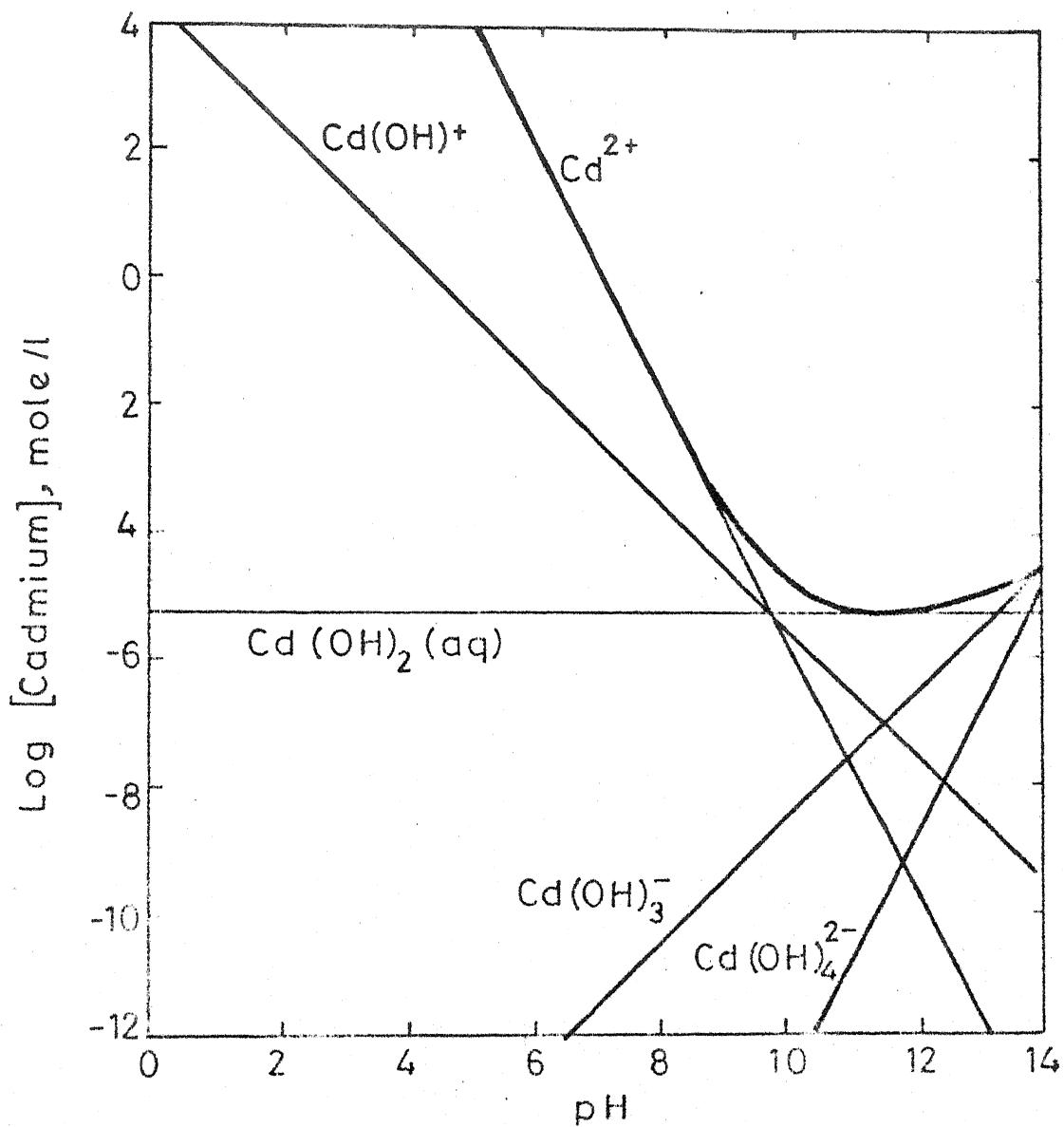
Fig.5·4 Stability Diagram of Cadmium
Hydroxide , Cd(OH)₂(S)

concentration and pH of water chemical precipitation of
cadmium hydroxide may occur. Thus solubility diagram gives
an idea about the extent of cadmium removed by hydrolysis
and subsequent removal of the remaining soluble cadmium by
sorbent. Cadmium is essentially present as divalent cation,
Cd^{2+}, upto pH 7.5 and as divalent cation Cd^{2+} and monovalent
cation $Cd(OH)^{+}$ in the pH range of 7.5 to 8.5. At pH higher
than 9.5 but below 11 the species present are decreasing
concentration of Cd^{2+} and increasing concentration of $Cd(OH)_2$ aq
vide Figure 2.1.

In order to relate sorption of cadmium as a function of
pH, the pH corresponding to net zero point of charge (pH_{zpc})
for the adsorbent was established. The pH_{zpc} of chitosan is
8.56.

At $pH < pH_{zpc}$ both sorbent and sorbate are positively
charged. Figures 5.2 and 5.3 show that significant amount of
cadmium was adsorbed below pH_{zpc}. As explained earlier, at
lower pH values H_3O^{+} ions compete with Cd^{2+} ions for the
adsorption sites. Above pH 3 to pH_{zpc}, as H_3O^{+} ions decrease,
rate and capacity of adsorption increase.

At $pH = pH_{zpc}$ to pH = 9 both adsorption rate and
capacity increased. Although at $pH = pH_{zpc}$, the net surface
charge of the sorbent is zero, but this does not mean that
surface is without any charged sites. According to Anderson
et.al. (1981) 30% of the total surface acidic sites may be
charged. At $pH > pH_{zpc}$, while the species of cadmium in
solution are still positively charged, the surface of sorbent

is negatively charged. This implies that, in addition to
electrostatic forces, specific chemical interaction must also
play an important role in cadmium adsorption. Huang and
Ostovic (1978) and Bhattacharya (1983) made these observations
for cadmium sorption on activated carbon and bituminous
Giridih coal respectively.

In the present study, cadmium concentration used for
pH effect is 2 mg/l and this concentration may cause some
precipitation of $Cd(OH)_2$ at pH 10. Hence, upto pH 9, removal
of cadmium is entirely due to adsorption process but at pH
10 remaining cadmium as $Cd(OH)_2$ (aq) is available for sorp-
tion.

Beyond pH 9, a decreasing trend in adsorption is shown
(Figure 5.3). Cadmium-hydroxy complexes which are formed at
this pH may be responsible for decrease in adsorption between
pH 9 and pH 10. Similar trend has been observed for Cd(II)
adsorption on soils (Elliot and Denneny, 1982), on Giridih
Bituminous coal and crushed coconut shell (Bhattacharya,
1983).

5.1.2 Effect of Chitosan/Cadmium Ratio

Figure 5.1 illustrates the effect of initial
cadmium concentration on adsorption. The adsorption density
increases by increasing the adsorbate concentration. This
is specially important for acidic pH values, for it is in
this region where the Cd^{2+} ions must compete with H^+ ions
for the available sites on the chitosan binding sites.

Figures 5.5 and 5.6 present data obtained from a different approach. In this case the chitosan dose was varied for the same initial cadmium concentration. Experiments were done at cadmium concentrations of 1.5 mg/l and 10 mg/l. These diagrams are useful in giving a clearer picture of possible optimum conditions for adsorption. For example, 92% cadmium removal is achieved at pH 6.5 when the chitosan/cadmium ratio is 250 (mg/mg) at initial concentration of cadmium 1.5 mg/l. However, 96% removal can be attained by keeping chitosan/cadmium ratio 333.3.

When cadmium concentration was increased to 10 mg/l, 97% removal was obtained at chitosan/~~carbon~~ cadmium ratio 150. In a separate experiment when 3 g ~~carbon~~ chitosan was added to 200 ml of 100 mg/l cadmium solution (Ch/Cd = 150), 99.4% cadmium adsorption was obtained. However, kinetically, the time to reach equilibrium reaction was slightly decreased with increasing Ch/Cd ratio.

At higher cadmium concentration Cd^{2+} ions get more binding sites on chitosan as H^+ ions remain constant at a particular pH. This provides improvement in cadmium adsorption.

5.1.3 Effect of Calcium Concentration on Cadmium Adsorption

Batch experiments were conducted to study the effect of calcium ions on sorption of cadmium by chitosan and results are shown in Figure 5.7. Concentration of calcium was 67 times more than cadmium but Figure 5.7 shows that there is very little effect of calcium ions on the adsorption of cadmium. Only 7% drop is observed in cadmium
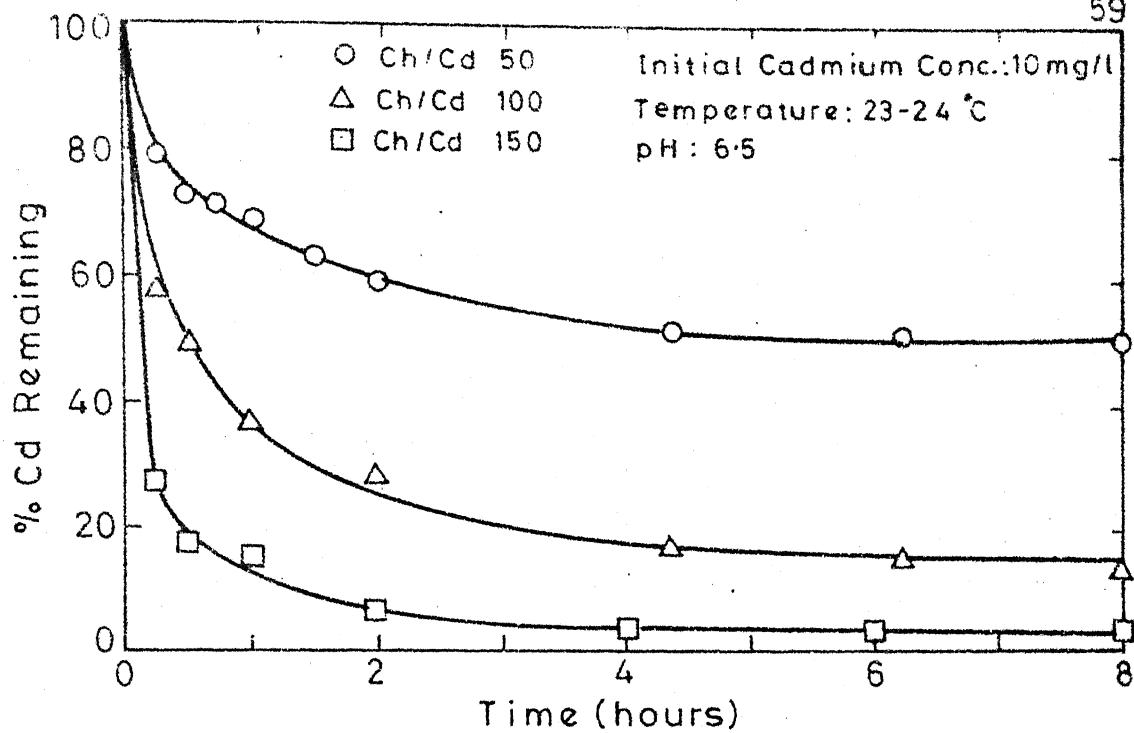
Fig.5.5 Kinetics of Cadmium Adsorption on Chitosan;
Effect of Ch/Cd Ratio (Cd=10 mg/l)
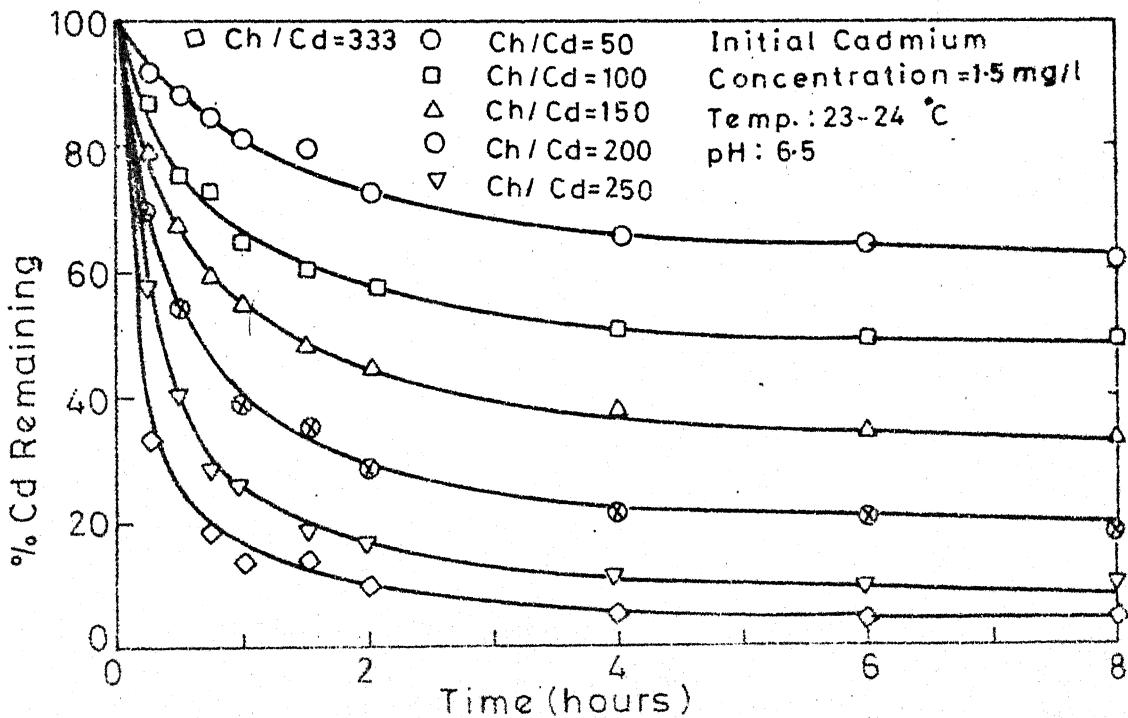
Fig.5.6 Kinetics of Cadmium Adsorption on Chitosan;
Effect of Ch/Cd Ratio (Cd=1.5 mg/l)

Initial Cadmium Concentration : 1·5 mg/l

Adsorbent Concentration : 500 mg/l

Temperature : 24 °C

pH : 6·5

○ 0 ppm Ca^{2+}

△ 100 ppm Ca^{2+}

% Cd Remaining

Time (hours)
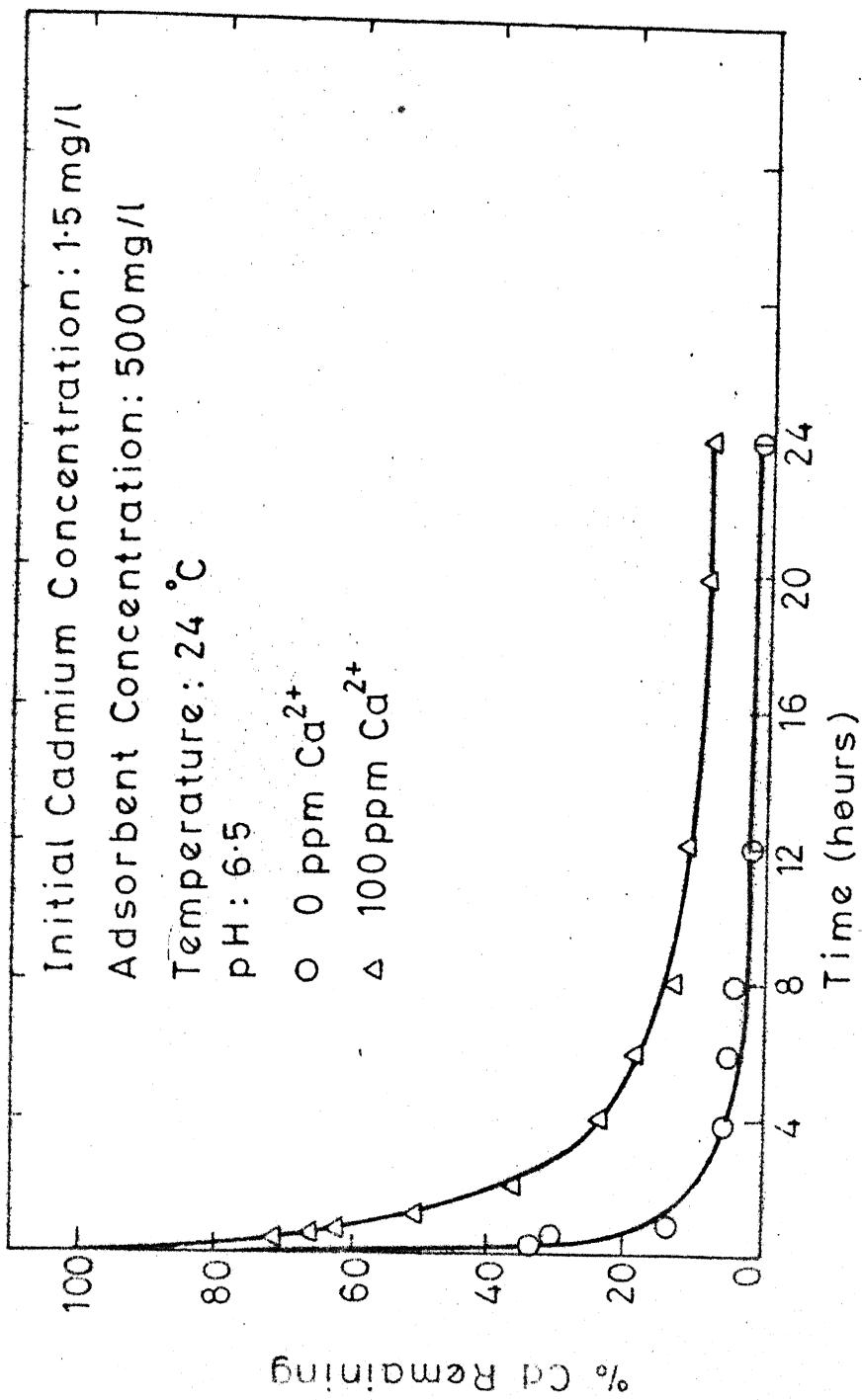
Fig. 5·7 Effect of Calcium on Sorption Kinetics of Cadmium on Chitosan

adsorption by chitosan in presence of calcium ions. Since calcium chloride was used for this experimental purpose, some chloride effect may be influential in reducing cadmium adsorption. Effect of chloride on adsorption of cadmium by chitosan is presented in Section 5.4.1. Earlier investigators have shown that chitosan does not adsorb sodium, potassium, calcium and magnesium (Muzzarelli et.al., 1970; Yaku and Koshijima, 1978). This is also confirmed in the case of calcium by Figure 5.7.

5.1.4 First Order Reversible Kinetic Model for Sorption of Cadmium

In the present section, attempts are made to fit the data of sorption kinetics into the first order equation in order to evaluate the rates of adsorption. A simple, overall reaction for sorption is assumed and is in the following form:
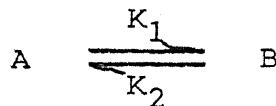
$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B \qquad\qquad 5.1$$

If the first order reversible model holds true, the rate equation for the reaction is expressed as

$$\frac{dC_B}{dt} = -\frac{dC_A}{dt} = C_{A_o} \cdot \frac{dX_A}{dt} = K_1 C_A - K_2 C_B$$

$$= K_1(C_{A_o} - C_{A_o} X_A) - K_2(C_{B_o} + C_{A_o} X_A) \qquad 5.2$$

where,

C_{A_o} = initial concentration of cadmium in solution,

C_{B_o} = initial concentration of cadmium on chitosan,

C_A = concentration of cadmium remaining in solution at any time t,

C_B = concentration of cadmium on chitosan at time t,

X_A = fractional conversion of cadmium, and

K_1, K_2 = first order rate constants.

At equilibrium conditions $K_1 = K_2$ and

$$\frac{dC_B}{dt} = \frac{dC_A}{dt} = 0 , \qquad\qquad 5.3$$

Hence,

$$X_{A_e} = \frac{K_C - C_{B_o}/C_{A_o}}{K_C + 1} \qquad\qquad 5.4$$

where,

X_{A_e} = fractional conversion of cadmium at equilibrium, and

K_C = equilibrium constant defined as:

$$K_C = \frac{C_{B_e}}{C_{A_e}} = \frac{C_{B_o} + C_{A_o} X_{A_e}}{C_{A_o} - C_{A_o} X_{A_e}} = \frac{K_1}{K_2} \qquad\qquad 5.5$$

where,

C_{A_e} = equilibrium concentration of cadmium in solution, and

C_{B_e} = equilibrium concentration of cadmium on chitosan.

The rate equation in terms of equilibrium conversion may be obtained from Equations 5.2, 5.4 and 5.5:

$$\frac{dX_A}{dt} = (K_1 + K_2)(X_{A_e} - X_A) \qquad\qquad 5.6$$

Integrating Equation 5.6 and substituting for K_2 from Equation 5.5 gives:

$$- \ln(1 - \frac{X_A}{X_{A_e}}) = K_1(1 + \frac{1}{K_C})t \qquad 5.7$$

Equation 5.7 can be rewritten in a different form with more physical meaning as follows:

$$\ln[1 - U(t)] = -K't \qquad 5.8$$

where K' is the first order overall rate constant. Further

$$K' = K_1(1 + \frac{1}{K_C}) = K_1 + K_2 \qquad 5.9$$

and

$$U(t) = \frac{C_{A_o} - C_A}{C_{A_o} - C_{A_e}} = \frac{X_A}{X_{A_e}} \qquad 5.10$$

$U(t)$ is called the fractional attainment of equilibrium (Helfferich, 1962).

Figure 5.8 shows initial 6 hour plots of $\ln[1 - U(t)]$ versus time as per Equation 5.8 for 5 and 10 mg/l initial cadmium concentrations. Figure 5.9 shows same type of plots for different pH values for 2 mg/l cadmium concentration. These plots indicate a straight line fit, justifying the validity of assuming first order reversible reaction. From Figures 5.8 and 5.9, it is observed that the straight line portions when extended do not pass through the origin indicating an initial high rate of cadmium uptake during the first 15 minutes. This indicates that some active sites exist on the external surface of the chitosan having high affinity for cadmium. This is same instantaneous adsorption
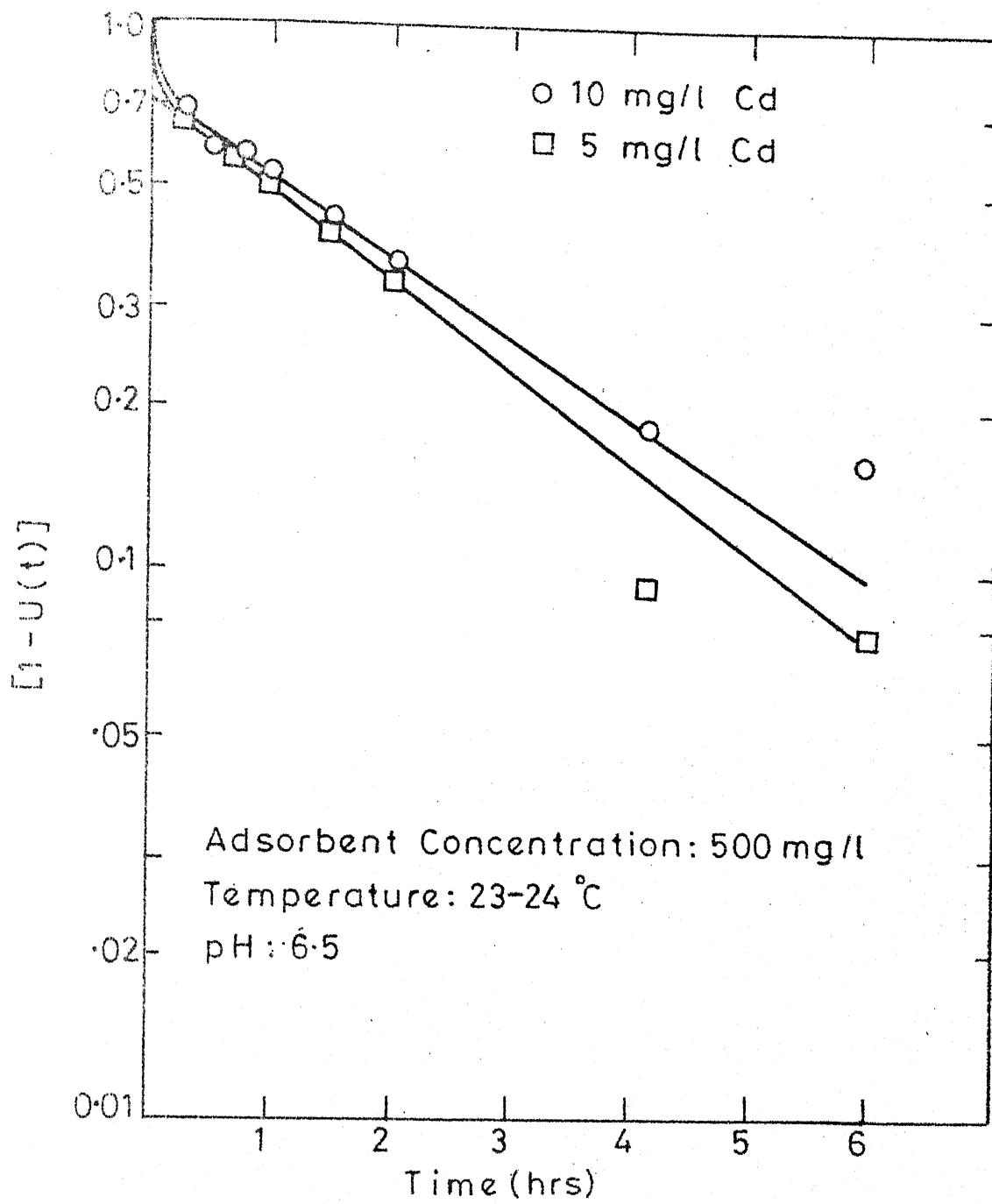
Fig 5.8 First Order Reversible Kinetic Fit
of Cadmium Adsorption Data on
Chitosan
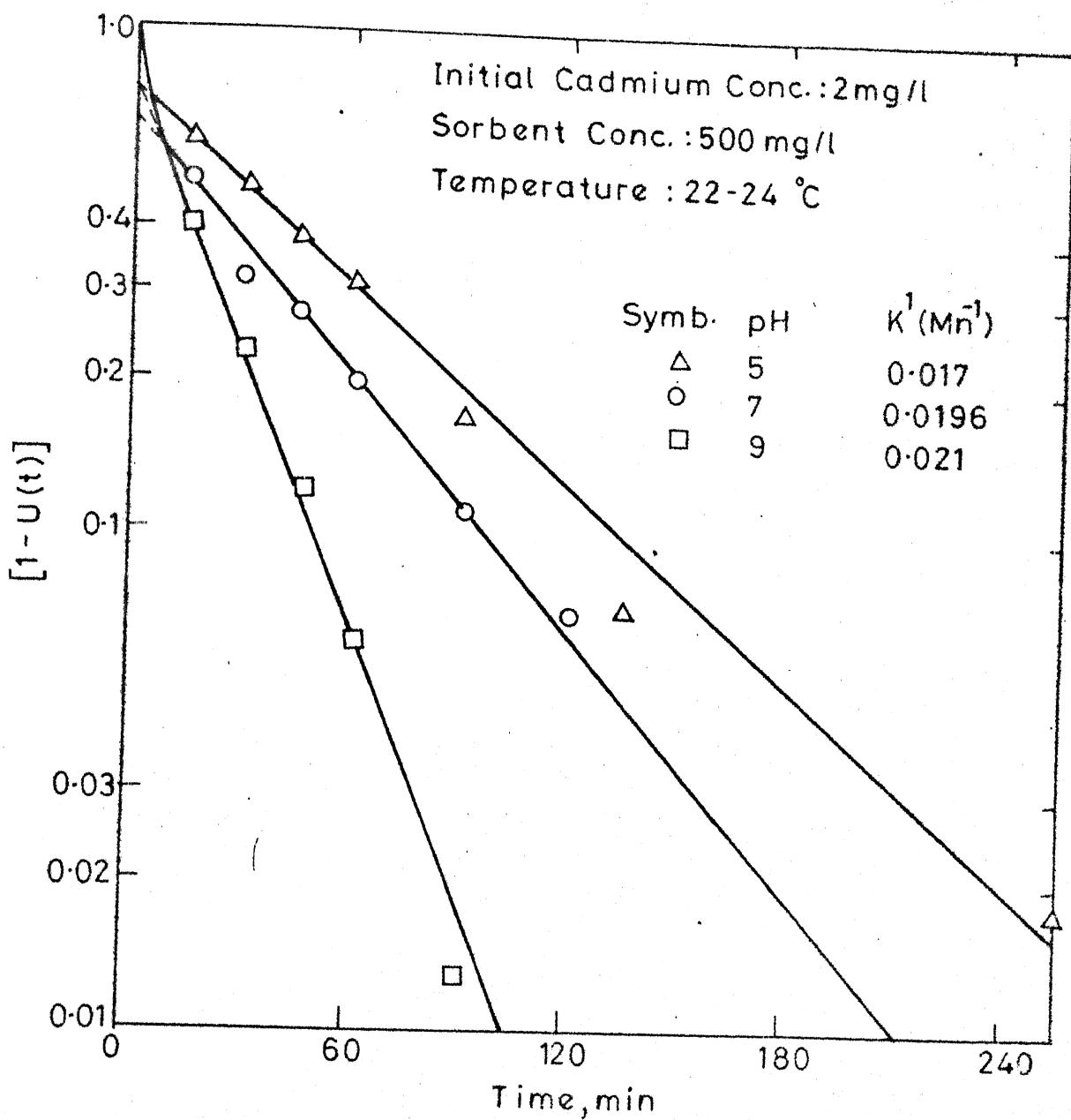
Fig. 5.9   First Order Reversible Kinetics Fit for Sorbent

Initial Cadmium Conc.: 2 mg/l
Sorbent Conc.: 500 mg/l
Temperature: 22-24 °C

Symb.	pH	$K^1(Mn^{-1})$
$\triangle$	5	0.017
$\bigcirc$	7	0.0196
$\square$	9	0.021

of cadmium on chitosan as indicated in Section 5.1. An

identical approach was adopted to evaluate rate of sorption

of inorganic mercury on hair (Michelson et.al., 1975) and of

cadmium on Giridih bituminous coal and crushed coconut shell

(Bhattacharya, 1983).

The values of K' were obtained from the slopes of the

first order reversible kinetic plots and those of K_C were

evaluated from equilibrium concentrations using Equation 5.5.

Subsequently K_1 and K_2 were calculated using Equation 5.9.

These values are presented in Table 5.1.

Table 5.1

The Values of Rate Constants (K', K_1, K_2) and K_C

Initial Cadmium Concentration mg/l	pH	K' per hour	K_C	K_1 per hour	K_2 per hour
10.0	6.5	0.3386	1.86	0.2202	0.1184
5.0	6.5	0.3872	9.00	0.3485	0.0387
2.0	5.0	0.9163	6.30	0.7907	0.1255
2.0	7.0	1.1760	11.50	1.0800	0.0941
2.0	9.0	2.4645	39.00	2.4028	0.0616

From the table, it can be observed that rate of forward

reaction K_1 (transfer rate of solute to the sorbent) is

generally higher for lower concentrations of cadmium and

higher pH values. The reverse reaction rate (transfer rate

of solute from sorbent to solution) is faster for higher
concentrations of cadmium and for lower pH values. This
implies that utilising maximum capacity of chitosan can give
better regeneration at lower pH values.

It can also be observed that as the ratio of chitosan
to cadmium increases, K_1 also increases. Thus, in order to
obtain higher rate of sorption, it is required to increase
chitosan concentration or decrease cadmium concentration.

5.2 Evaluating the Rate Limiting Step in Cadmium Sorption

Whenever sorption is suggested as a unit process for
wastewater treatment, it is essential to have information
concerning rate determining step in sorption so that appro-
priate facilities may be furnished accordingly in the full-
scale plant. Efforts are made to evaluate the rate limiting
step.

There are three consecutive steps in the process of
adsorption of a solute material from the solution by a porous
sorbent. These are:

1. The transport of adsorbate through a surface film to
   the exterior of the adsorbent (film diffusion step).

2. Adsorption on the exterior surface and diffusion of
   the adsorbate into the pores of the adsorbent (pore
   diffusion step).

3. Adsorption of the adsorbate into the interior surface
   of the adsorbent (intraparticle transport step).

The first two steps are known as the transport pheno-
mena while the third step is known as the attachment pheno-

Several methods are used to determine the rate limiting step. Pore diffusion and film diffusion controlled processes differ in their rate laws and are dependent on the particle size, solution concentration, temperature and degree of agitation (Table 5.2). The dependence on the variables of the experimentally observed data can help to investigate the rate controlling mechanism. Studies were conducted on these lines.

Table 5.2

Dependence of Transfer Rate on Experimental Conditions (Helfferich, 1962)

Parameter	Pore Diffusion Control	Film Diffusion Control
1. Sorbate concentration	No effect	C*
2. Particle size	$\dfrac{1}{r_o^2}$	$\dfrac{1}{r_o^{**}}$
3. Rate of agitation	No effect	Increases with agitation rate
4. Temperature	Increases with temperature, 4 to 8% per °C	Increases with temperature, 3 to 5% per °C

* Sorbate concentration

** Radius of the sorbent particle.

5.2.1 Effect of Sorbate Concentration

As shown by Weber and Morris (1963), the kinetic experimental data for different initial concentrations can be used to establish the rate limiting step in the sorption

process. Weber and Morris (1963) used $t^{1/2}$ instead of t to find out the variation in the amount of sorbate sorbed with $t^{1/2}$. Figure 5.10 shows the amount of cadmium sorbed per gram of chitosan against $t^{1/2}$ for 1, 1.5, 2, 5 and 10 mg/l initial cadmium concentrations. To some extent plots are showing the same general shape, i.e., an initial curved portion, a linear section followed by a final curved section. For such type of plots, it can be considered that the particles are being surrounded by a boundary layer film through which the cadmium molecules must diffuse prior to external adsorption on the sorbent surface, and this particular step is responsible for the initial curvature. However for lower concentrations of cadmium initial portion of the plots is showing straight line. The linear portion of the plots is governed by pore diffusion mainly in the rate controlling step. As the bulk concentration of cadmium starts decreasing, the final portion of the plots begins to curve and attains saturation due to a decrease in the rate of diffusion (Alexander et.al., 1978).

A rate parameter, K, defining the slope of the linear portion of the plot is determined and the values are presented in Table 5.3.

Although these K values do not have normal dimensions of rate, their relative values are very useful under similar conditions for rate parameters. Therefore K/C values were calculated and are presented in Table 5.3.
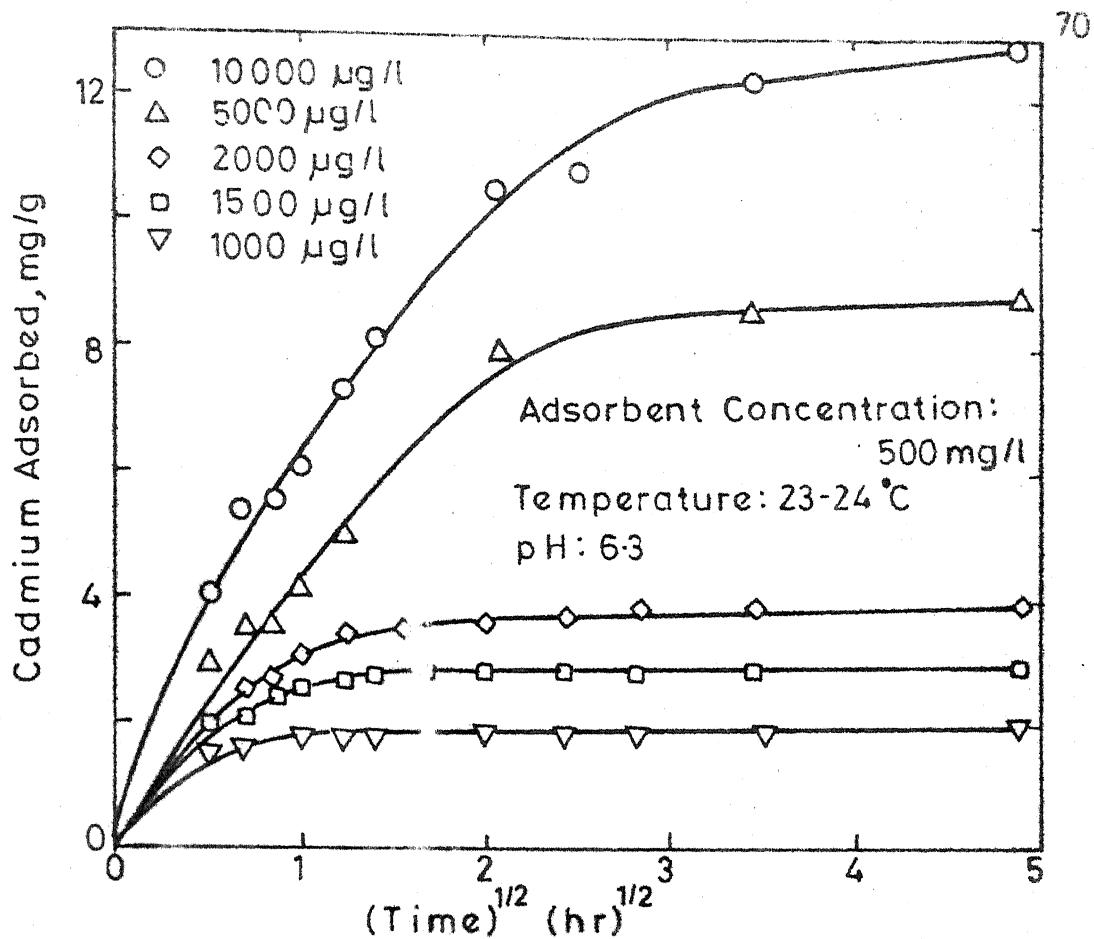
Fig.5·10 Cadmium Adsorbed against (Time)$^{1/2}$ for Different Initial Concentrations on Chitosan
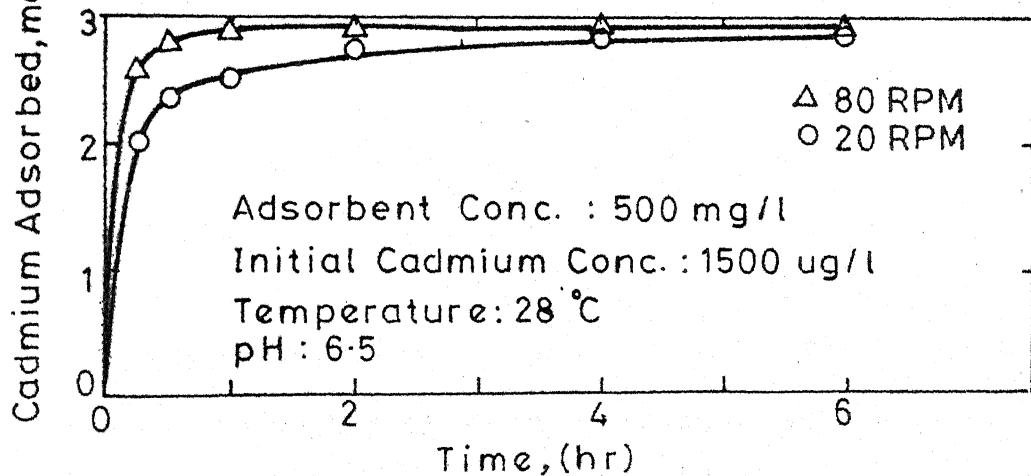
Fig. 5.11 Effect of Rate of Agitation on Cadmium Adsorption

Table 5.3

Rate Parameter, K, as a Function of Initial Cadmium Concentration

Initial Cadmium Concentration, C (mg/l)	Rate Parameter K (mg g^{-1} hr$^{-1/2}$)	K/C
10.0	6.2	0.62
5.0	4.3	0.86
2.0	3.1	1.55
1.5	2.55	1.70
1.0	1.8	1.80

From the Table 5.3, it can be observed that the rate parameter, K, varies with initial cadmium concentration. For film diffusion to be rate limiting K/C values should remain constant as per Table 5.2. However, there is large variation in K/C values. Thus, it seems that film diffusion is not the rate limiting step. For higher cadmium concentrations, a large portion of the plots are straight lines, thus pore diffusion seems to be predominant in this case.

5.2.2 Effect of Rate of Agitation

Figure 5.11 shows the effect of agitation rate on the rate of adsorption of cadmium by chitosan. For first two hours, the rate of cadmium uptake is very much increased by increasing the rate of agitation. However, final uptake of cadmium at both the rates of agitation varies slightly; greater uptake of cadmium at higher rate of agitation. The increase in cadmium uptake with rate of

agitation indicates the rate limiting step of film diffusion.

This method seems to be less reliable because the solution may have attained its limiting hydrodynamic efficiency, so that an increase in the agitation rate can remain without effect on the uptake rate even if the rate limiting step is film diffusion.

5.2.3 Effect of Particle Size

Figure 5.12 shows the plots of the amount of cadmium adsorbed per gram of sorbent (adsorption density) against $t^{1/2}$ for four different particle sizes and a constant initial cadmium concentration of 1500 µg/l. The curves show an initial linear portion followed by a curved portion. The K values have been obtained from the linear portion of the curves and are presented in Table 5.4. For pore diffusion controlled processes the parameter K should vary reciprocally with the second power of the diameter of the sorbent particles (Weber and Morris, 1963). According to them, this relationship is also applicable for porous sorbents when the rate of transport to internal surface areas is controlled by the external resistance, i.e., film transport.

Table 5.4 shows that rate of sorption increases with decrease in the sorbent size. However less difference is found in final sorptive capacity as shown in Figure 5.12. This may be due to lower initial concentration of cadmium (1500 µg/l).

Figure 5.15 demonstrates that the sorption-rate of cadmium-chitosan system varies linearly with the reciprocal
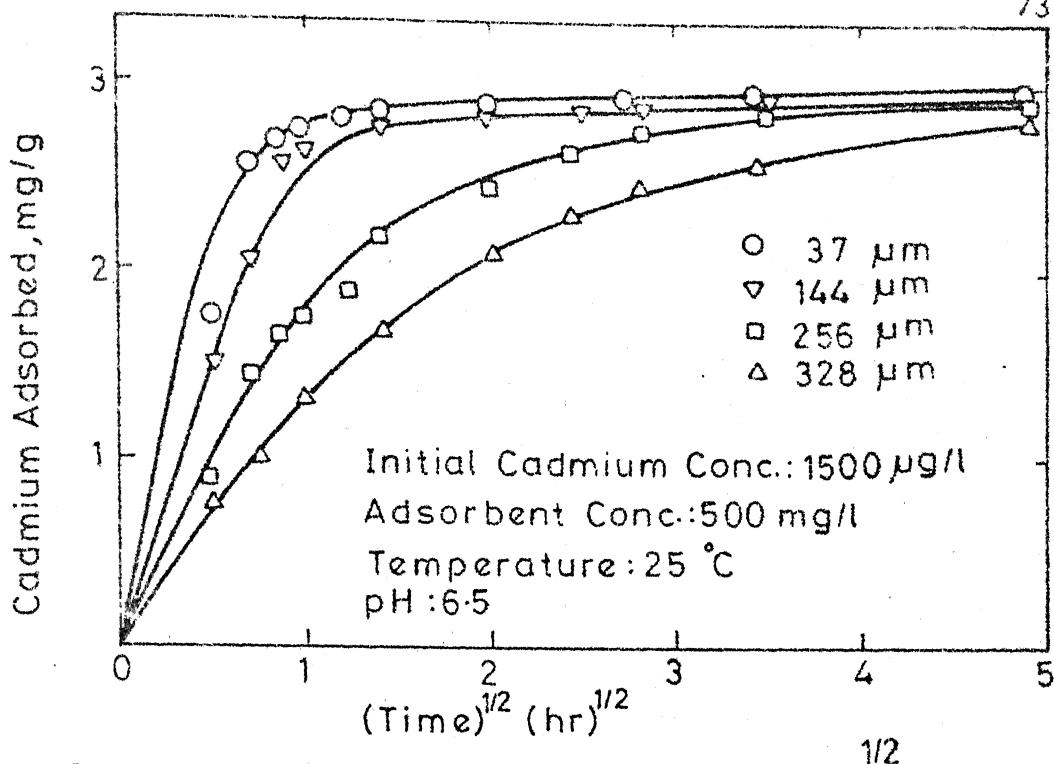
Fig.5·12 Cadmium Adsorbed against (Time)$^{1/2}$ for different Particle sizes of Chitosan
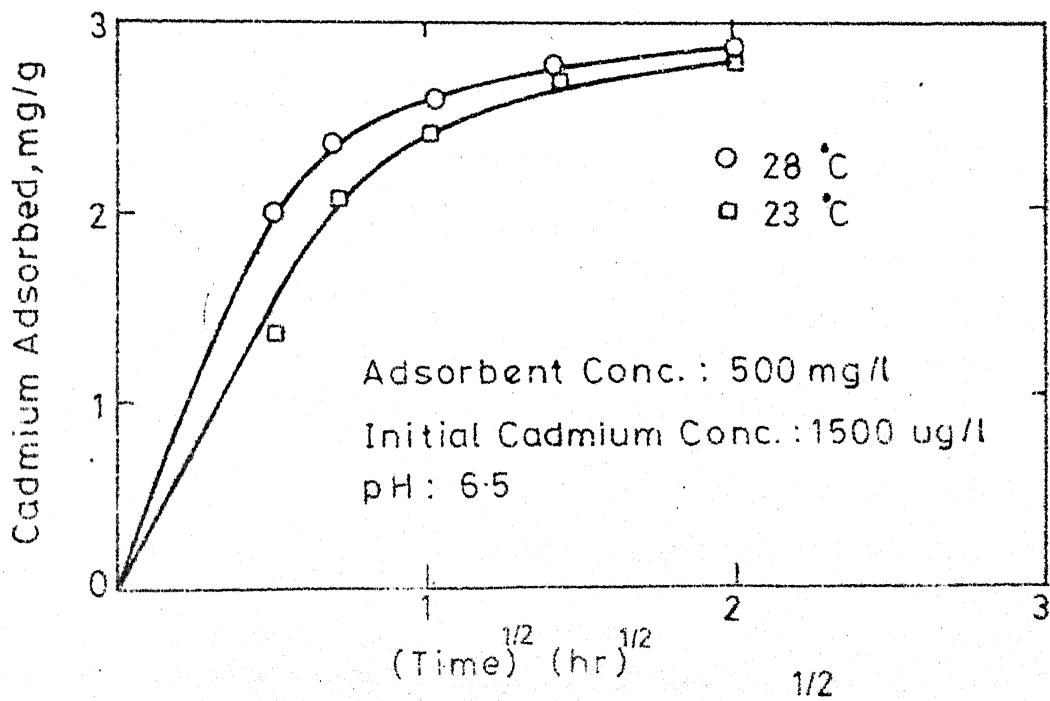
Fig.5·13 Cadmium Adsorbed Vs (Time)$^{1/2}$ for Chitosan on Different Temperatures

Table 5.4

Rate Parameter, K, as a Function of Particle Size

Geometric Mean Size of Particle, d (μm)	Initial Cadmium Concentration (mg/l)	Rate Parameter, K (mg g^{-1} $hr^{-1/2}$)
37	1.5	2.8
144	1.5	2.53
256	1.5	1.83
328	1.5	1.3

of the second power of chitosan geometric mean size (G_m). This indicates pore diffusion of the rate limiting step in cadmium-chitosan adsorption system.

5.2.4 Effect of Temperature

The temperature dependence of cadmium adsorption onto chitosan is demonstrated in Figure 5.13. The results show an increase in adsorption for an increase in temperature. Adsorption, being a mass transfer process, is a strong function of temperature. However, the temperature effect on adsorption generally are not felt to be significant over the range of temperature generally faced in water and wastewater treatment.

Figure 5.13 shows a percentage increase in rate of sorption of 5.8% per °C. As per Table 5.2, pore diffusion appears to be rate limiting step.

To know the nature of sorption, the temperature dependence of sorption reaction can be observed by comparing the

activation energies. The increase in the rate of reaction with increasing temperature can be described as

$$K = A\, e^{-E/RT} \qquad 5.11$$

where, K = specific rate constant

A = a temperature-independent factor sometimes called the frequency factor,

E = minimum activation energy (KJ/mole) that reaction system must have for reaction to occur,

R = gas constant (KJ/mole/°K), and

T = temperature (°K).

With moderate temperature ranges the value of A and E may be considered to remain constant. In logarithmic form, the equation can be written as:

$$\ln K = \ln A - E/RT \qquad 5.12$$

indicating that linear relation should occur between lnK and 1/T. The slope of the straight line fitting the plot is -E/2.303 R.

The plot of rate of adsorption as per Equation 5.12 is presented in Figure 5.14. The activation energy for chitosan was calculated to be 37.2 KJ/mole. The activation energy is high enough for physico sorption but not significantly high to conclude the reaction as chemisorption. Activation energy in the case of ion exchange is generally low and lies within 20 Kcal/mole. For chemisorption it should be in the range of 40-400 KJ/mole. Consequently the
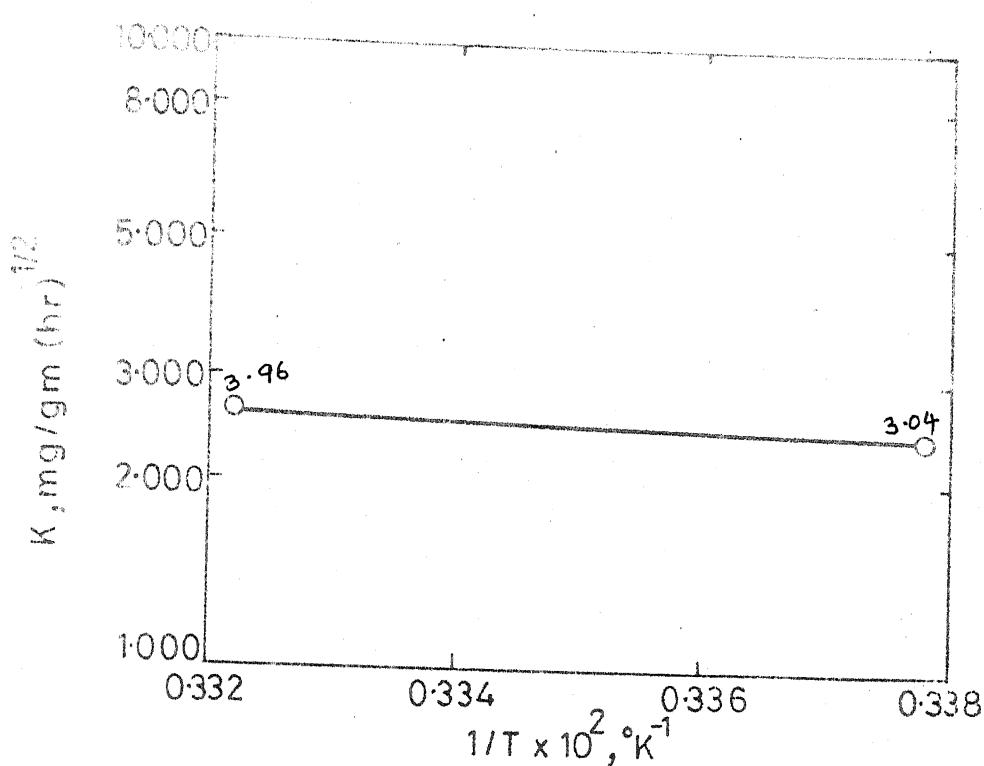
Fig.5·14 Effect of Temperature on the Rate of Adsorption
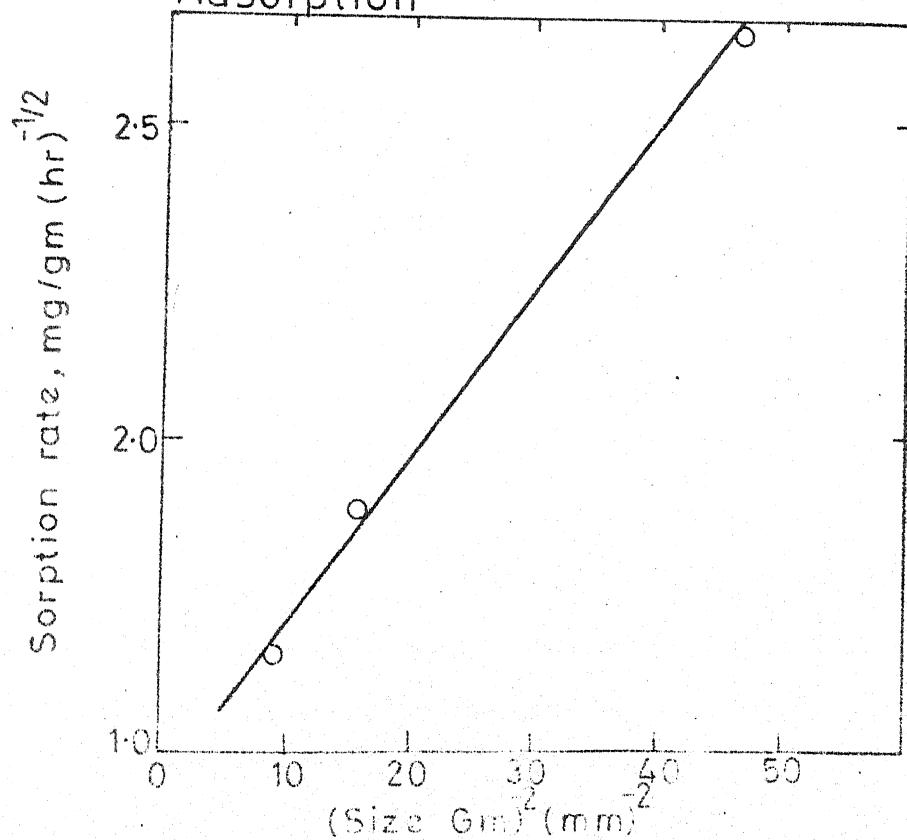
Fig.5·15 Effect of Size on the Rate of Adsorption

ion exchange-cum-physi-sorption. The value for Giridih coal-cadmium   system was found to be 36.6 KJ/mole (Bhattacharya, 1983) and same nature of sorption was explained by him.

5.2.5 Summary

Various experimental investigations were done to understand the rate limiting step of chitosan-cadmium adsorption system. Table 5.5 presents the summary of all the results of rate limiting step experiments.

Table 5.5

Summary of the Results of Various Tests Performed to Determine the Rate Limiting Step

Test	Pore Diffusion	Film Diffusion
1. Sorbate concentration	Slightly significant	—
2. Particle size	Significant	—
3. Rate of agitation	—	Significant
4. Temperature	Significant	

From Table 5.5 it may be said that cadmium adsorption is rate limited by pore diffusion in the case chitosan-cadmium system. For a batch type contact operation, which provides a higher degree of agitation or mixing, pore diffusion is often the rate limiting step. However, there appears to exist a complex combination of operative mechanisms rather than the reaction being governed by a single operative mechanism.

5.3 Sorption Equilibria

A sorption equilibrium is established when the concentration of contaminants in bulk solution is in dynamic balance with that of the interface, i.e., an equal number of molecules desorb as adsorb in a given time.

Saturation curves (sorption isotherms) for cadmium sorption on chitosan are presented in Figure 5.16 for different particle sizes.

The observed increase in capacity for the smaller particle sizes may be because (1) smaller particles more closely approach a true equilibrium than do the larger particles, (2) a greater portion of the total pore volume is available to adsorb molecules in smaller particles. It is not likely that such large differences were entirely due to different degrees of equilibrium after 24 hours of contact. Rather, there seems to be a true capacity difference for the different particle sizes. It is also likely that the activity and adsorption capacity of chitosan particle decreases with distance from its external surface as a result of reduced accessibility of its inner regions. If the particle size preparation process simply grinds away external surface to produce small particles, these latter particles may represent a more active portion of the original chitosan. These effects require further examination.

5.3.1 Sorption Isotherms

The linearised sorption isotherms are the most convenient and informative way of representing the experi-
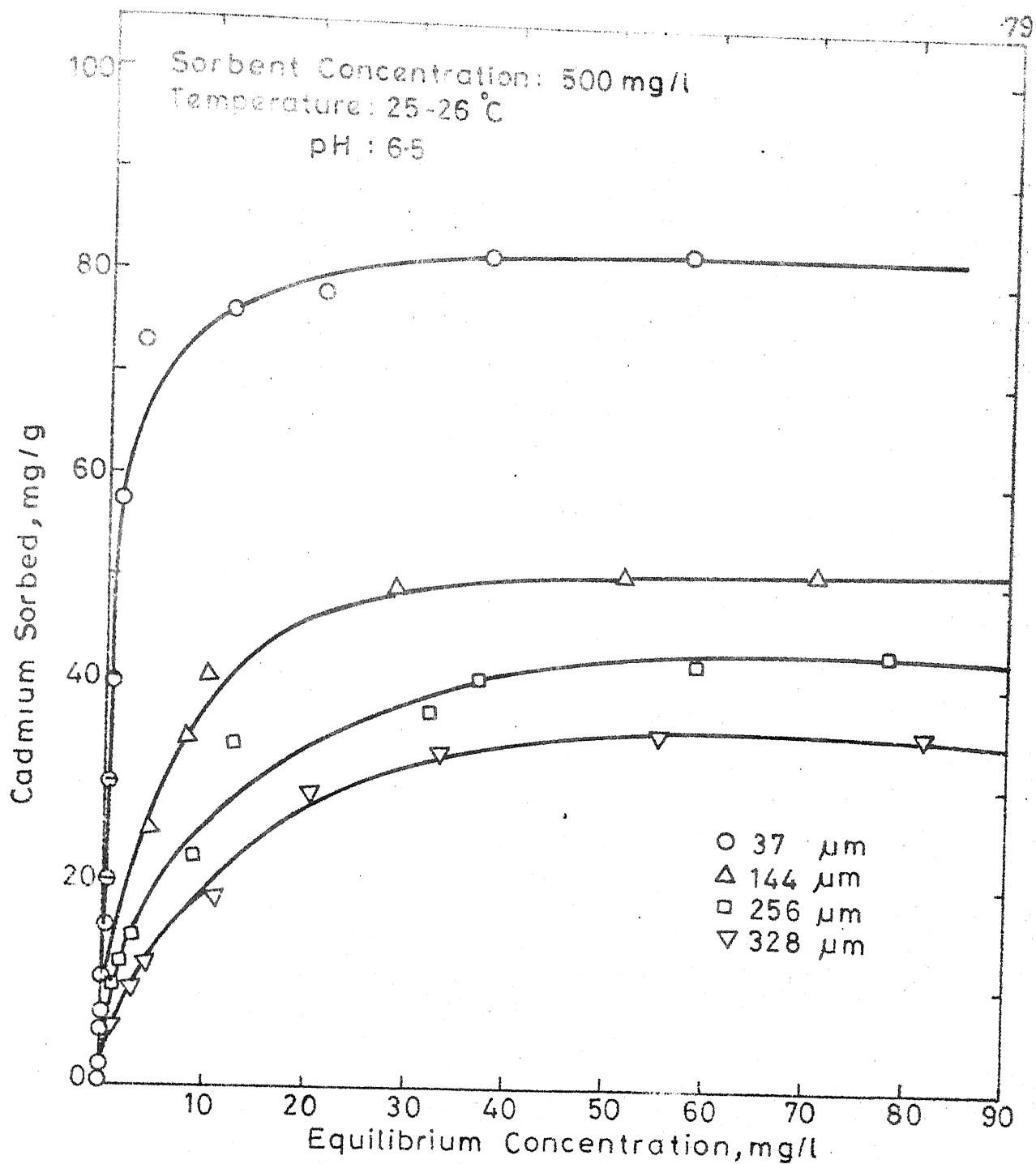
Fig. 5·16   Saturation Curves for Cadmium Sorption

heterogeneous surface energies in which the energy term in
the Langmuir equation varies as a function of surface
coverage, X/M, strictly due to variation in heat of sorption
(Adamson, 1967). Freundlich equation has been found to be
more adaptable to sorption data than the theoretically derived
Langmuir equation. Majority of sorption processes do not
comply with the first assumption on which the Langmuir equa-
tion is based. A complete monolayer is not usually formed in
the sorption of solutes from solution.

The general form of Freundlich's isotherm is

$$q_e = X/M = KC_e^{1/n} \qquad 5.13$$

in which,

q_e = X/M = the equilibrium surface concentration (weight
        of cadmium sorbed per unit weight of chitosan),

K = a constant which is related to sorption capacity,

C_e = the equilibrium concentration in solution, and

1/n = a constant which is related to adsorption intensity.

The above equation is converted to the following linearized
form

$$\log \frac{X}{M} = \log K + \frac{1}{n} \log C_e$$

which gives a straight line with a slope of 1/n and an
intercept equal to the value of logK for C_e = 1 (log C_e = 0).
Freundlich equation generally agrees quite well with the
Langmuir equation and experimental data over moderate range
of concentration. Unlike the Langmuir equation, however,

it does not express X/M as a linear form of C at low concentrations nor does it agree very well at high concentrations, since n must reach some limit when the surface is fully covered.

The sorption data for various sizes of chitosan fitted into the logarithmic form of the Freundlich equation is presented in Figure 5.17. The values of various constants of Freundlich's isotherm along with the sorptive capacities are presented in Table 5.6 for different sizes of chitosan.

Table 5.6

Freundlich Parameters for Adsorption of Cadmium on Different Sizes of Chitosan

Size m	Slope 1/n	Intercept log K mg/g	Adsorptive capacity, K mg/g
37	0.7648	1.7482	56.0
144	0.5873	1.1238	13.3
256	0.5535	0.9685	9.3
328	0.5119	0.8062	6.4

The Freundlich's equations for different sizes of chitosan are as follows (Table 5.7).

It may be noted that the adsorptive capacity is important in selecting and specifying a suitable sorbent system. More the sorptive capacity of a sorbent, better the combination since service time of sorption column will
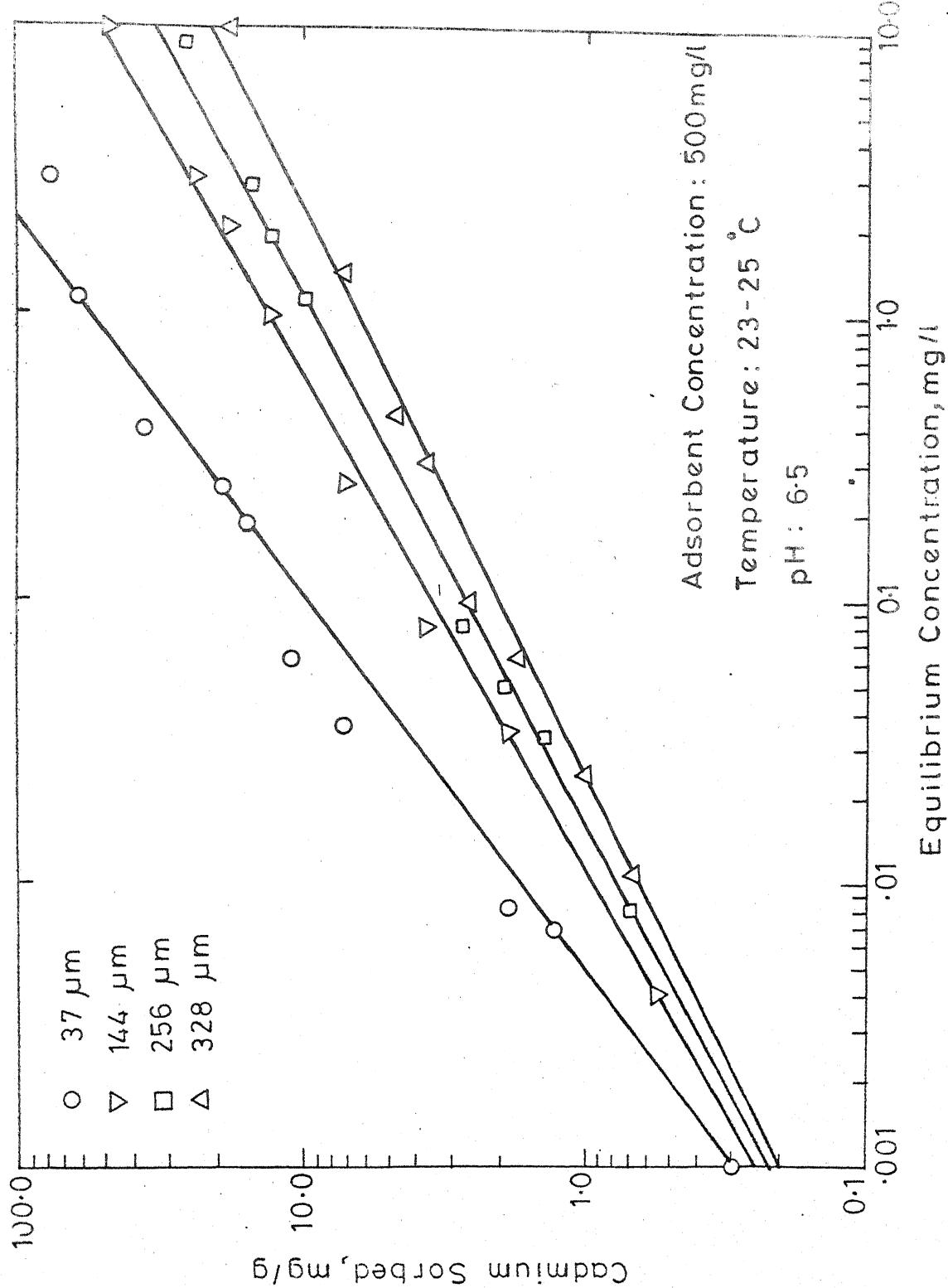
Fig. 5.17 Linearised Sorption Isotherm

Table 5.7

Freundlich's Equations for Different Sizes of Chitosan

Size μm	Freundlich Equation	
37	$56.0 \, c^{0.7648}$	5.14
144	$13.3 \, c^{0.5873}$	5.15
256	$9.3 \, c^{0.5535}$	5.16
328	$6.4 \, c^{0.5119}$	5.17

be more. From the data obtained it can be observed that smaller particle size chitosan (37 μm) is much superior to all other particle sizes. Bhattacharya (1983), in case of Giridih coal and crushed coconut shell for removal of cadmium, found K values as 3.321 and 2.123 and 1/n values as 0.475 and 0.497 respectively.

The isotherm data can be used to calculate the ultimate sorption capacity of chitosan by substituting the equilibrium concentration in Freundlich equation. For 328 μm particle size 6.4 mg/g cadmium can be adsorbed when equilibrium concentration is 1 mg/l. It means one gram of chitosan can treat 1.48 litres of water when initial cadmium concentration is 5 mg/l. Visualising high sorptive capacity of chitosan, it is certainly economical to go in for this natural polymer, since chitosan is N-deacetylated product of chitin which is a waste product from fish industries. This can also solve the disposal problem of waste products of fish industries.

Within the indicated range of cadmium levels, n > 1 implies that the rate of cadmium uptake increases with increase in cadmium concentration, indicating intensive accumulation.

5.4 Effect of Chloride, Ionic Strength, Zinc and EDTA on Cadmium Sorption

5.4.1 Effect of Chloride Concentration

Effect of chloride on cadmium sorption was investigated using a wide range of chloride concentration. This is significant as cadmium forms various chloro-complexes depending upon pH and chloride concentration. Figure 5.18 shows the effect of chloride concentration on cadmium adsorption by chitosan. It can be observed that cadmium adsorption was not affected even by a chloride concentration of 1000 mg/l (as Cl^-) showing only a slight decrease in adsorption in comparison to non-chloride pure system. Reduction in cadmium adsorption was 10.7% when chloride concentration was raised from zero to 1500 mg/l. We may consider the reaction in the presence of chloride.

1. The NH_2 group in chitosan acts as a weak base and a proton is added in aqueous solutions, creating a NH_3^+ group. Since the pH of the initial cadmium solution was 6.5, majority of the amino sites were protonated at this pH. The protonation occurs very rapidly and accounts for the behaviour of chitosan as a cationic polyelectrolyte in aqueous solutions.

2. The positive charge of the NH_3^+ site prevents Cd^{2+}
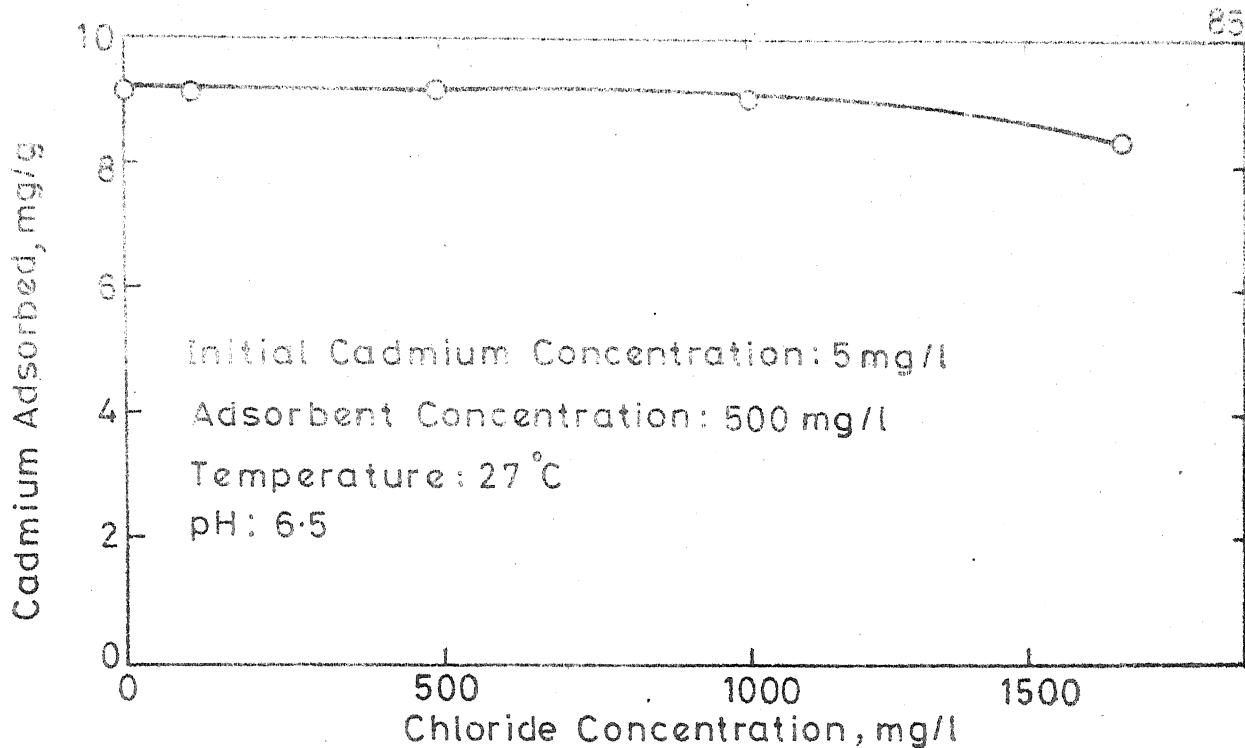
Fig.5·18 Effect of Chloride Concentration on Cadmium
Adsorption
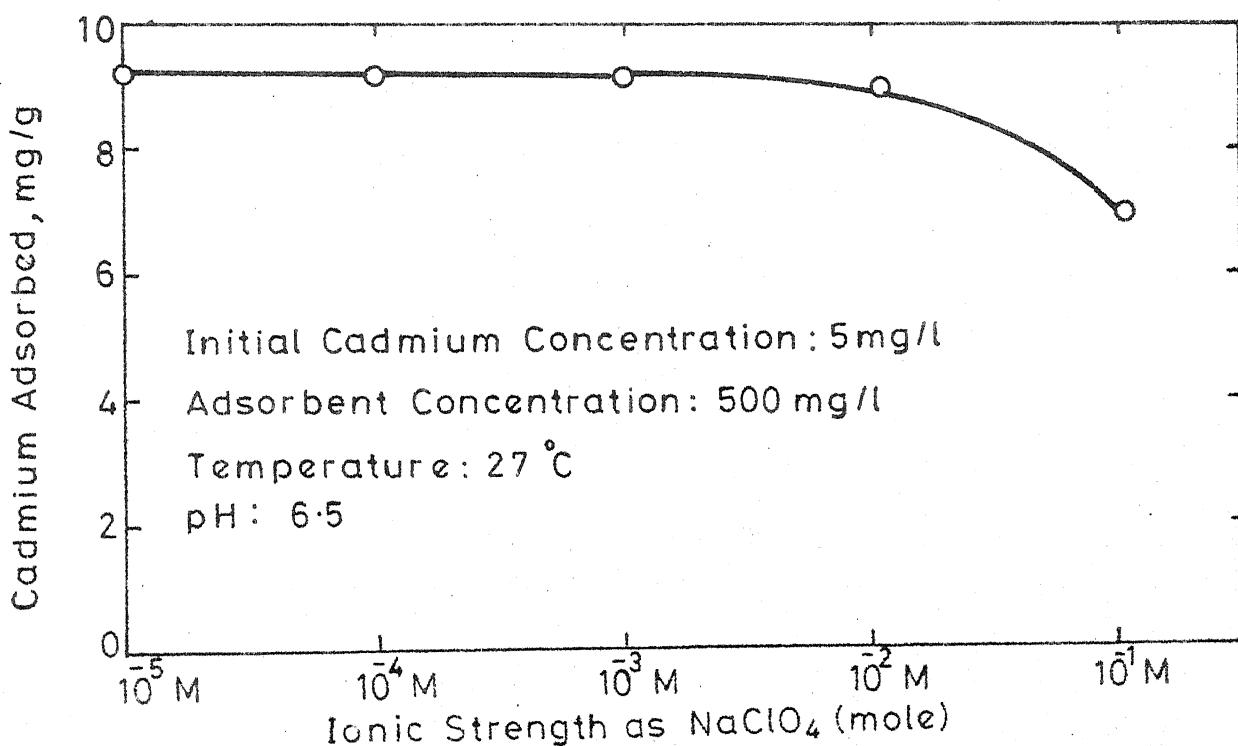
Fig.5·19 Effect of Ionic Strength on Cadmium
Adsorption

enters readily, probably forming NH_3^+ - Cl groups. The salt formation neutralizes the charge on the ammonia groups and the cadmium ions are now able to enter the chitosan.

3.   The cadmium ion is attracted to the electron pair associated with the nitrogen, forming a strong covalent bond and preventing the unprotonated amino groups from being protonated. The chloride group will then bond ionically to the cadmium-amino complex in order to neutralise the positive charge introduced by the cadmium ion.

The rate at which cadmium can enter chitosan is thus determined by the rate at which chloride enters the polymer and this is in turn is governed by the equilibrium between the protonated amino group and the chloride ion. Same hypothesis was presented by Averbach (1982) for the interaction of anions and cations with chitosan in case of copper sulfate.

At higher chloride concentrations (above 10^{-3} M), there is a reduction in Cd^{2+} species due to formation of soluble chloro complexes like $CdCl^+$, $CdCl_2$ and $CdCl_3^-$ (Figure 2.2). The observed decrease in sorption indicates that these species have lesser affinity for sorbents.

5.4.2   Effect of Ionic Strength

Figure 5.19 shows the influence of ionic strength on the adsorption of cadmium onto chitosan. Data were obtained for five different molar concentrations of background electrolyte, ranging from 10^{-5} to 10^{-1} M. The

results indicate that when ionic strength was increased from 10^{-5} to 10^{-2} M, adsorption capacity decreased only by 2.17%. A sudden decrease in adsorption capacity was observed when ionic strength was changed from 10^{-2} to 10^{-1} M. A decrease of 22% in the cadmium uptake capacity was observed in this case.

That the extent of adsorption is sensitive to changes in concentration of supporting electrolyte indicates that electrostatic attraction may be a significant component of the overall adsorption in this system. The electrostatic free energy, G_{elect}, contributes to the total free energy of adsorption, G_{ads}, and depends on the ionic strength of solution. This term is given as (Huang and Smith, 1981):

$$G_{elect} = z F \Psi_d$$

where,

z = the ionic charge,

F = the Faraday constant, and

Ψ_d = the potential in the plane of the adsorbing ion. When the ionic strength is increased, the electrical double layer around the adsorbate cadmium ion is compressed, which leads to a decrease in the electrostatic potential, Ψ_d. The result is a reduction in the coulombic free energy, and consequently a decrease in cadmium adsorption.

5.4.3 Effect of Co-ion Concentration (Zn^{2+})

Figure 5.20 shows the effect of zinc concentration on cadmium uptake by chitosan. An increase in Co-ion
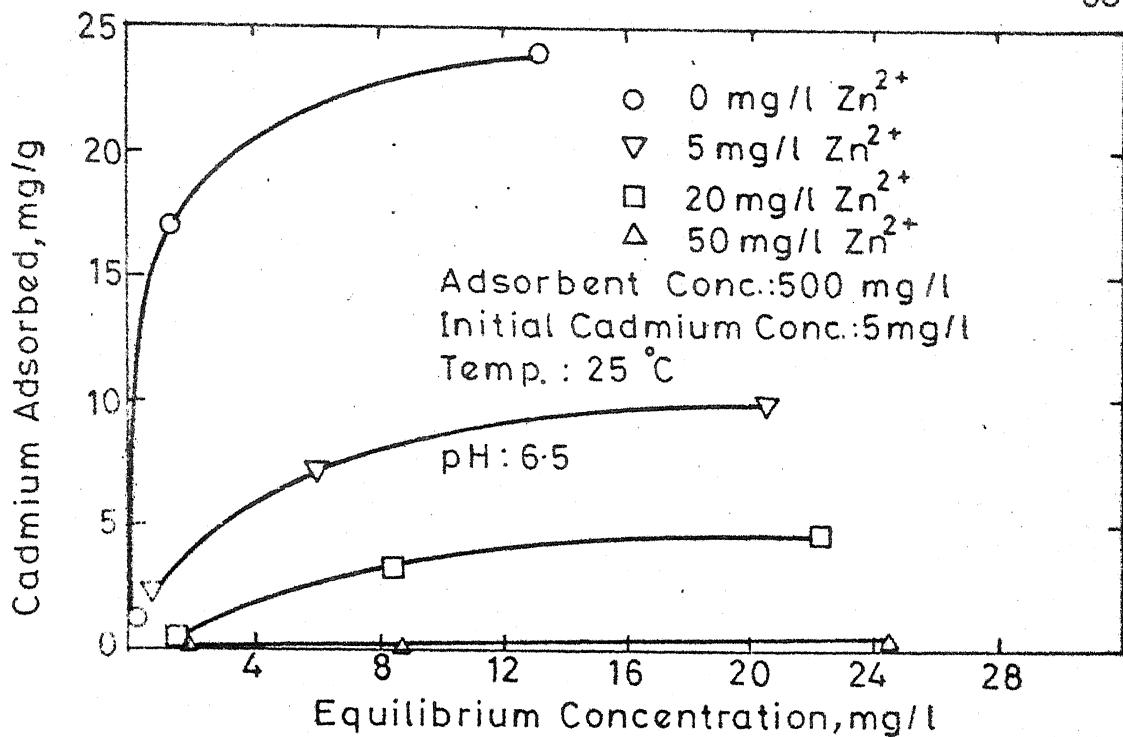
Fig.5·20 Chitosan – Zinc – Cadmium Competitive
Equilibrium Isotherms
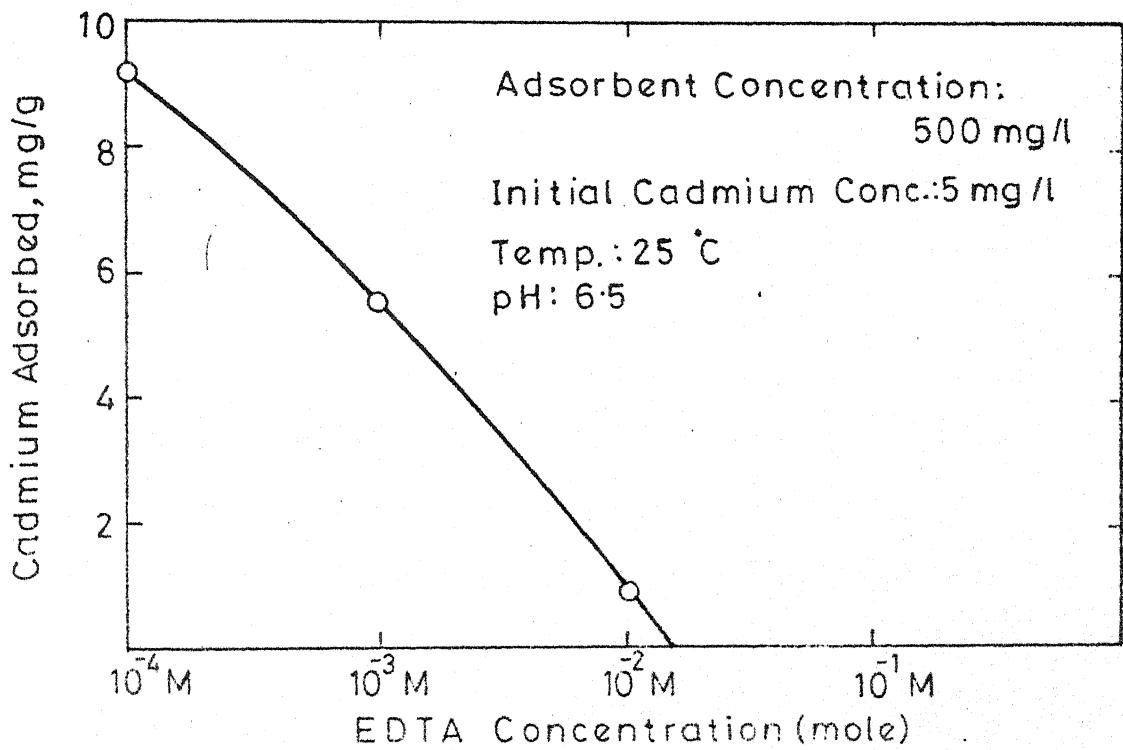
Fig.5·21 Effect of EDTA on Cadmium Adsorption

loading on chitosan. This behaviour can be interpreted as the result of the more effective competition of the zinc ions. The zinc ion uptake by chitosan in the presence of cadmium seems to be high. Zinc complexation by chitosan has been documented in the literature (Muzzarelli et.al., 1970).

5.4.4 Effect of Chelating Agent (EDTA)

The effect of chelating agent such as EDTA on the cadmium adsorption capacity of chitosan is shown in Figure 5.21. EDTA has significant effect on cadmium adsorption. Cadmium adsorption decreased to zero when EDTA concentration was changed from 10^{-4} to 10^{-1} M. At EDTA concentration of 2.5×10^{-2} M, cadmium adsorption did not take place. This may be due to greater affinity of EDTA to chitosan than cadmium.

5.5 Desorption and Regeneration

Regeneration of the exhausted chitosan is essential if the chitosan adsorption is to be made more economically feasible in practice. To gain some idea in the reversibility of the adsorption reaction and possibilities for regeneration, desorption experiments were conducted.

Following a two-hour adsorption period, cadmium-laden chitosan was separated from solution and put into another solution of distilled water at the same pH and temperature. Figure 5.22 shows the amount of cadmium released back into solution by the chitosan after two hours of reaction.

The obvious trend in the data is that the percentage desorbed increases with decreasing pH. This is expected,

cadmium decreases with decreasing pH. About 85% desorption
occurs at pH 3. However, percent desorption values at low
pH cannot be regarded as meaningful due to the very small
extent of adsorption there.

One clear indication from the desorption data of chito-
san is that regeneration may be accomplished by treating the
chitosan with strong acid. The addition of small amounts of
acid would strip the cadmium from the surface of the carbon,
and hopefully retain the metal in a form that is concentrated
enough for useful recovery.

No desorption of cadmium took place at pH 10, indica-
ting the ineffectiveness of alkalies in regenerating chitosan.

5.5.1 Batch Desorption Studies

Desorption kinetic studies of cadmium were con-
ducted in redistilled water and also in 0.01 N HCl. The
results are presented in Figure 5.23. About 5.5% desorption
of cadmium took place in redistilled water, whereas, 88%
desorption was observed in 0.01 N HCl. The rate of desorption
was found to be similar to that of adsorption, in the sense
that the maximum level of cadmium desorbed was attained in
1 hour for both distilled water and 0.01 N HCl.

Low desorption of cadmium from loaded chitosan in
redistilled water conceivably represents the fraction
rather loosely bound to the chitosan. This further indi-
cates that the major portion of the sorbed cadmium is
possibly bound to the chitosan through stronger interaction
involving the surface functional groups of the chitosan.
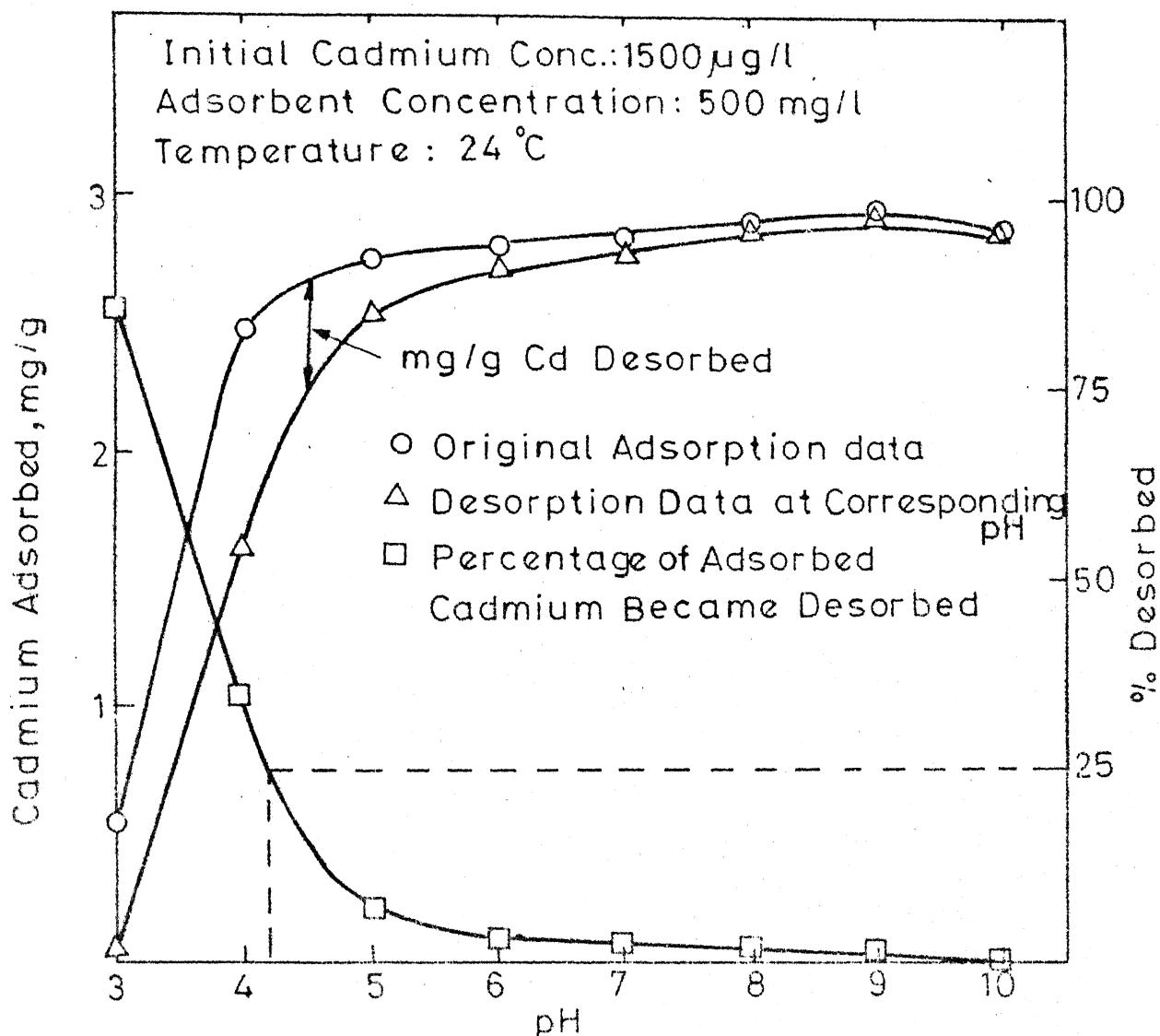
Fig. 5.22 Extent of Desorption of Cadmium as Affected by pH
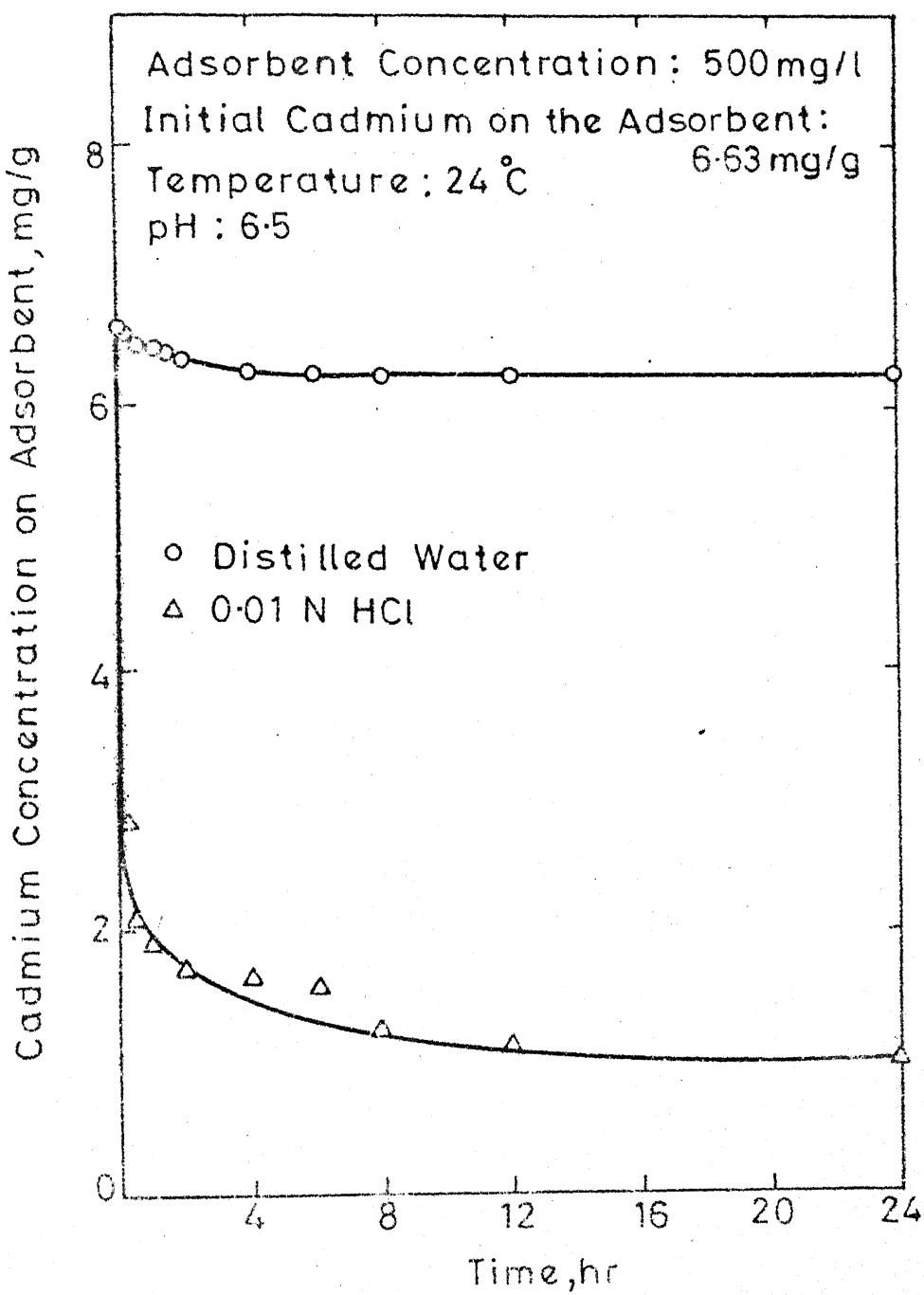
Fig 5·23 Desorption Kinetics on Chitosan

Desorption in redistilled water was done at pH 6.5 which is below pH_{zpc}. At this pH both sorbent and sorbate are positively charged. This gives an indication of ion exchange sorption. Desorption by 0.01 N HCl further confirms this. The small portion of sorbed cadmium not recoverable by regeneration indicates that cadmium which is bound through even stronger interactions.

Desorption was also conducted in 0.1 M EDTA and positive result was obtained. 0.1 M EDTA desorbed 95% of cadmium loaded on chitosan.

Cycles of regeneration and loading of the cadmium-chitosan system was investigated for their practical utilisation. Table 5.8 gives the material balance calculations for regeneration experiments using 0.01 N HCl.

Table 5.8

Material Balance Calculations for Regeneration of Chitosan with 0.01 N HCl

Number of Cycles	1	2	3
Amount of cadmium on chitosan from previous cycle (mg/g)	0 0	252	260
Amount of cadmium adsorbed by chitosan in loading cycle (mg/g)	2966	2178	1263
Total amount of cadmium going into recovery cycle (mg/g)	2966	2430	1523
Amount of cadmium recovered in recovery cycle (mg/g)	2714	2170	1237
Amount of cadmium remaining on chitosan (mg/g)	252	260	286
Percentage recovery of cadmium	91.5	89.3	81.2

Cadmium recovery in the first regeneration cycle was 91.5%, but it was observed that cadmium loading decreased suddenly in the next two cycles. Inspite of good percentage recovery in all the three cycles, adsorption of cadmium went on decreasing. It was observed that there was some reduction in weight of chitosan after desorption in 0.01 N HCl, indicating that chitosan dissolves to some extent in HCl. The reduced amount of chitosan may be the cause of less adsorption in next two cycles. Since chitosan does not dissolve in sulfuric acid, experiments are needed to be done for desorption studies in sulfuric acid. In this study sulfuric acid was not tried for this purpose.

Muzzarelli and Rocchetti (1974) found partial removal of mercury from chitosan after the first cycle by sulfuric acid, whereas, 15 ml of 10 mM potassium iodide solution removed 100% mercury from a 6 x 1 cm column containing 1 g of chitosan for more than 10 cycles. He also found potassium cynide solution suitable for the removal of mercury from chitosan.

In the case of cadmium-chitosan system also, search of another efficient regenerant is required, however, no further study was taken in this regard in the present work.

5.6 Column Studies

In a column type continuous flow operation the rate of adsorption depends upon the concentration of the solute in the sorbate. In this operation the sorbent is continuously in contact with a fresh sorbate and consequently the concentration in the solution in contact with given layer of the sorbent in the column is relatively constant.

Adsorption isotherms cannot possibly furnish accurate scale-up information since:

(1) Adsorption in a flow column is not at equilibrium.

(2) The sorbent would not become totally exhausted in a commercial process before regeneration.

(3) Uneven flow patterns throughout the column would result in incomplete exhaustion of the bed.

Consequently, it is necessary to carry out flow test using column prior to obtaining design models. An initial cadmium concentration of 5 mg/l was used in tap water system. The performance of chitosan column is presented in Figure 5.24. A flow rate of 3 M^3/M^2/day was maintained manually. The effluent cadmium concentration was found zero just in one hour. Some leakage of cadmium was found before that. After 25 hours effluent started giving cadmium concentration but at very low values. Effluent cadmium concentration of 1 mg/l was found after 77 hours. Thus, 23.1 litres of cadmium spiked tap water was treated by the column having 16.5 g of chitosan. To prevent any precipitation due to cadmium carbonate formation, pH of influent was reduced to 6.9 with 0.1 N HCl in this study. Tap water treated per gram of chitosan is 1.4 l/g which is in fair agreement with sorption isotherm data of 1.48 l/g with 328 μm size. However, size used for column study was 378 μm, thus showing an improvement in adsorption capacity in the case of column study. In sorption isotherm equilibrium concentration in effluent is fixed, while in the case of column study it varies from
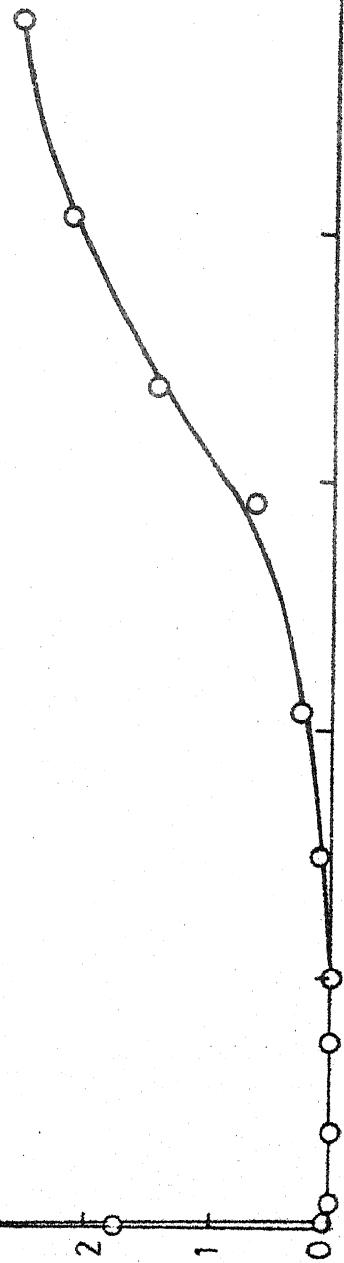
Fig. 5·24 Performance of Chitosan Column for Cadmium Tap water System

zero to 1 mg/l (mostly zero). This also indicates improve-
ment in adsorption by using continuous flow process.

It is apparent from Figure 5.23 that time taken to
reach the effluent concentration to acceptable limit is very
less (half an hour) thus showing the applicability of the
system. Other competitive ions in the tap water did not
influence the cadmium adsorption capacity of chitosan. This
is very much helpful in treating cadmium polluted water
and wastewater by chitosan.

Dimensions of the columns also affect optimum results.
Muzzarelli and Rocchetti (1974) have reported that column
containing 7.5 times more chitosan purified thirteen times
more water. Thus, not only the amount of chitosan but also
the dimensions of the columns must be taken into account for
optimum results.

6. CONCLUSIONS

Based on the findings of the present investigations, the following conclusions may be drawn:

(1) Cadmium may be adsorbed appreciably from industrial effluents, mine waters or other water supply using chitosan, a natural polymer.

(2) The kinetics of adsorption were very favourable indicating maximum adsorption level reaching within first hour of contact of chitosan with cadmium solution.

(3) The pH of the system can affect cadmium adsorption to some extent. Cadmium uptake by chitosan increases linearly from pH 4 to pH 9, after which it shows a decreasing trend. At pH 3 adsorption was only 18%.

(4) Chitosan to cadmium ratio (Ch/Cd) has an effect on the rate of adsorption and equilibrium adsorption capacity. Increasing Ch/Cd increases the equilibrium cadmium adsorption capacity and the initial removal rate. However, the time to attain equilibrium remained same. Increased cadmium concentration needed lowered Ch/Cd ratio for effective removal.

(5) Significant adsorption was observed at pH_{zpc} and below this implying that specific chemical interaction plays a substantial role in cadmium uptake by chitosan.

(6) Sorption kinetic data can be described as first order reversible reaction.

(13) Downflow column study indicated the practical appli-
cability of chitosan for removal of cadmium. The
column was found effective in removing cadmium from
an initial concentration of 5 mg/l to zero value at a
flow rate of 3 $M^3/M^2/hr$.

7. SUGGESTIONS FOR FUTURE WORK

The present investigation reveals that chitosan is an effective adsorbant for cadmium removal. Further works based on this investigation may be carried out on the following guidelines:

(1) It may be feasible to develop a relative affinity series of metals because such series would help in selecting usefulness of chitosan where there may be competition of various metals for binding sites on chitosan.

(2) Further studies may be conducted using actual cadmium polluted wastewater to evaluate the actual design parameters.

(3) Extensive column operations may be carried out for cadmium and other heavy metals sorption by

    a. Changing the dimensions of the column

    b. Using various sizes of chitosan

    c. Changing the direction of flow

    d. Changing flow rates of the influent containing cadmium.

(4) Search of an efficient regenerant for cadmium-chitosan system is required.

(5) Other derivatives of chitin and chitosan such as chitin phosphate, chitosan phosphate, chitosan sulfate etc. may be tried for metal uptake ability.

8. ENGINEERING SIGNIFICANCE

The results of the laboratory investigation on removal of cadmium by chitosan presented and discussed here have indicated the potential usefulness of chitosan in removing cadmium from water. Due to its high cadmium adsorption capacity chitosan may be employed for cadmium control in surface and ground water as well as for removal of cadmium from cadmium-laden wastewater.

The reported upper limits of cadmium in surface and ground water are about 300 and 100 $\mu g/l$, respectively whereas the recommended upper limit of cadmium in drinking water is 10 $\mu g/l$. A cadmium containing ground water supply may be effectively treated using a chitosan adsorption column. For a surface water supply where a municipal water treatment plant exists, powdered chitosan may be employed as a coagulant aid with alum. Alternatively, for both ground as well as surface water powdered chitosan may be used as a coagulant in small-scale household water purification. It may be noted here that usefulness of chitosan as coagulant for water clarification has been recently demonstrated by Vaidya and Bulusu (1984).

For cadmium-laden wastewater, chitosan may also be eff-ectively employed for cadmium removal. Both the modes of application, e.g., adsorption column as well as an additive with conventional coagulants like aluminium or iron salts seem feasible. The mode of application will be governed by the characteristics of the wastewater under consideration.

REFERENCES

Adamson, A.W. (1976). Physical Chemistry of Surface. (3rd ed.) Interscience Publishers, Inc., New York.

Alaxander, F., Poots, V.J.P., and McKay, G. (1978). Adsorption Kinetics and Diffusion Mass Transfer Processes During Color Removal from Effluent Using Silica. Industrial and Engineering Chemistry - Process Design and Development, 17, pp. 406-410.

Anderson, M., Bauer, C., Hansmann, D., Loux, N., and Stanforth, R. (1981). Expectations and Limitations for Aqueous Adsorption Chemistry. In: Adsorption of Inorganics at Solid-Liquid Interface. Anderson, M.A., and Rubin, A.J. (Eds.), Ann Arbor Science Pub., Inc.

Argo, D.G., and Culp, C.L. (1972). Heavy Metals Removal in Wastewater Treatment Processes. Water and Sewage Works, 119, pp. 62-65, 128-132.

Averbach, B.L. (1982). The Interaction of Anions and Cations with Chitosans. Proceedings of the Second International Conference on Chitin/Chitosan. Hirano, S., and Tobura, S. (Eds.), The Japanese Society of Chitin and Chitosan, Sapporo, Japan, pp. 248-251.

Axberg, C., Wennerburg, M., and Stenius, P. (1980). Flocculation of Waste Emulsions Using Polyelectrolytes. Water Pollution Research and Development (Part 1). Jenkins, S.H. (Ex. Ed.), IAWPR/Pergamon Press.

Aylett, B.J. (1979). The Chemistry and Bioinorganic Chemistry of Cadmium. In: The Chemistry, Biochemistry and Biology of Cadmium. Webb, M. (Ed.), Elsevier/North Holland Biomedical Press.

Barnes, D., Bliss, P.J., Gould, B.W., and Vallentine, H.R. (1981). Water and Wastewater Engineering Systems. A Pitman International Text.

Barrow, M.L., and Weber, J. (1972). Trace Element in Sewage Sludge. Journal of Science, Food and Agriculture, 23, pp. 93-110 (Quoted by Peterson and Alloway, 1979).

Barrows, H.L. (1966). Soil Pollution and its Influence on Plant Quality. Journal of Soil Water Conservation, 21, pp. 211-216.

Benjamin, M.M., and Leckie, J.O. (1981b). Soil Pollution and its Influence on Plant Quality. Journal of Soil Water Conservation, 21, pp. 211-216.

Benjamin, M.M., and Leckie, J.O. (1981b). Conceptual Model for Metal-Ligand-Surface Interactions During Adsorption. Environmental Science and Technology, 15, pp. 1050-1056.

Benjamin, M.M., and Leckie, J.O. (1982). Effect of Complexation by Cl, SO_4 and S_2O_3 on Adsorption Behaviour of Cd on Oxide Surfaces. Environmental Science and Technology, 16, pp. 162-170.

Besselieure, E.B., and Schwartz, M. (1976). The Treatment of Industrial Wastes. (2nd ed.) McGraw Hill, Inc.

Bhatia, M.N., Breidenback, W., and Waston, R.F. (1979). Treatability of Priority Pollutants: Status Review and Case Histories. Water-1979, American Institute of Chemical Engineers Symposium Series, 76, pp. 25-36.

Bhattacharya, A.K. (1983). Removal of Cadmium from Water by Low Cost Adsorbents. Ph.D. Thesis, Indian Institute of Technology, Kanpur, India.

Browning, E.M.D. (1969). Toxicity of Industrial Metals. (2nd ed.) London: Butterworth and Company.

Bachauer, M.J. (1973). Contamination and Vegetation Near a Zinc Smelter by Zinc, Cadmium, Copper and Lead. Environmental Science and Technology, 7, pp. 131-135.

Cadmium and the Environment: Toxicity, Economy, Control (1975). Organisation for Economic Cooperation and Development, Paris, France.

Carlstorm, D. (1952). J. Biophy. Biochem. Cyt., 3, p. 669 (Quoted by Saito et.al., 1982).

Chaney, R.L., and Hundemann, P.T. (1979). Use of Peat Moss Columns to Remove Cadmium from Wastewater. Journal Water Pollution Control Federation, 51, pp. 17-21.

Cheng, M.H., Patterson, J.W., and Minear, R.A. (1975). Heavy Metals Uptake by Activated Sludge. Journal Water Pollution Control Federation, 47, pp. 362-377.

Chizhikou, D.M. (1966). Cadmium. Translated by Hayler, D.E., Pergamon Press, Oxford, London.

Chou, E.J., and Okamato, Y. (1976). Removal of Cadmium Ion from Aqueous Solutions. Journal Water Pollution Control Federation, 48, pp. 2747-2752.

Controlling Pollution from the Manufacturing and Coating of Metal Products (1977). Water Pollution Control. EPA Technology Transfer Seminar Publication, United States.

Coombs, T.L. (1979). Cadmium in Aquatic Organisms. In: Chemistry, Biochemistry and Biology of Cadmium. Webb, M. (Ed.) Elsevier/North-Holland Biochemical Press.

Criteria Document - "Cadmium" (1977). Interim Draft No. 11, U.S., E.P.A.

Culp, G.L., and Culp, R.L. (1974). New Concepts in Water Purification. Van Nostrand Reinhold Co., New York.

Davies, P.H. (1976). The Need to Establish Heavy Metal Standards on the Basis of Dissolved Metals. In: Workshop on Toxicity to Biota of Metal Forms in Natural Water. Published by the International Joint Commission, Windsor, Ontario, Canada, pp. 93-126.

Dean, J.G., Bosqui, F.L., and Lanouetter, K.H. (1972). Removing Heavy Metals from Wastewater. Environmental Science and Technology, 6, pp. 518-522.

Dowdy, R.H., and Larsen, W.E. (1975). The Availability of Sludge-Borne Metals to Various Vegetable Crops. Journal Environmental Quality, 4, p. 278.

Elinder, C.G., Kjellstrom, T., Lind, B., Molander, M.L., and Silander, T. (1978). Cadmium Concentrations in Human Liver, Blood, and Bile, Comparison with a Metabolic Model. Environmental Research, 17, pp. 236-241.

Elliot, H.A., and Denneny, C.M. (1982). Soil Adsorption of Cadmium from Solutions Containing Organic Ligands. Journal of Environmental Quality, 11, pp. 658-663.

Epstein, E., and Chaney, R.L. (1978). Land Disposal of Toxic Substances and Water Related Problems. Journal Water Pollution Control Federation, 50, pp. 2037-2042.

Fleischer, M., Sarofim, A.F., Fossett, D.W., Hammond, P., Shacklette, H.T., Nisbet, I.C.T., and Epstein, S. (1974). Environmental Impact of Cadmium; A Review by the Panel on Hazardous Trace Substances Environmental Health Prospect, pp. 253-323.

Florence, T.M. (1977). Trace Metal Species in Fresh Waters. Water Research, 11, pp. 681-687.

Forstner, U., and Wittmann, G.T.W. (1979). Metal Pollution in the Aquatic Environment. Springer-Verlag, Berlin, Heidelberg, New York.

Friberg, L., Piscator, M., and Nordberg, G. (1971). Cadmium in the Environment. CRC Press, Cleveland.

Friberg, L., Piscator, M., Nordberg, G.F., and Kjellstrom, T. (1974). Cadmium in the Environment. (2nd ed.) CRC Press, Cleveland.

Gardiner, J. (1974). The Chemistry of Cadmium in Natural Water. I. A Study of Cadmium Complex Formation Using the Cadmium Specific Ion Electrode. Water Research, 8, pp. 23-30.

Giles, C.H., MacEwan, T.H., Nakhwa, S.N., and Smith, D. (1960). Studies on Adsorption: A System of Classification of Solution Isotherm. Journal of the Chemical Society, 3, p. 3973.

Gunn, S.A., and Gould, T.C. (1957). Proc. Soc. Exp. Biol. Med., 96, 820-823 (Quoted by Samarawickrama, 1979).

Hammons, A.S., Huff, J.E., Braunstein, H.M., et al. (1978). Reviews of Environmental Effects of Pollution. IV. Cadmium. ORNL-EIS-106. Oak Ridge National Laboratory, Tenn. (Quoted by Roberts, 1983).

Haque, M.A., and Subramanian, V. (1982). Copper, Lead and Zinc Pollution of Soil Environment. Criteria Reviews in Environmental Control, 12, pp. 13-68.

Helfferich, F. (1962). Ion Exchange. McGraw Hill Book Company, Inc., New York.

Henderson, R.W., Andrews, D.S., Lightsey, G.R., and Poonawala, N.A. (1977a). Reduction of Mercury, Copper, Nickel, Cadmium and Zinc Levels in Solution by Competitive Adsorption Onto Peanut Hulls and Raw Aged Bark. Bulletin Environmental Contamination and Toxicology, 17, pp. 355-359 (Quoted by Larsen and Schierup, 1981).

Henderson, R.W., Lightsey, G.R., and Poonawala, N.A. (1977b). Competitive Adsorption of Metal Ions from Solutions by Low-Cost Organic Materials. Bulletin Environmental Contamination and Toxicology, 18, pp. 340-344 (Quoted by Larsen and Schierup, 1981).

Henke, G., Sachs, H.W., and Bohm, G. (1970). Arch. Toxicology, 26, pp. 8-16 (Quoted by Samarawickrama, 1979).

Hindin, E., Denstan, G.H., and Bennett, R.J. (1968). Water Reclamation by Reverse Osmosis. Bulletin 310, Technical Extension Service, Washington State University, Pullman, Washington.

Hirano, S., Kondo, Y., Fuketa, M., and Yamashita, A. (1982). Structure and Properties of Some Chitosan-Halogen Complexes. Proceedings of the Second International

Conference on Chitin and Chitosan. Hirano, S., and Tokura, S. (Eds.), The Japanese Society of Chitin and Chitosan, Sapporo, Japan, pp. 57-62.

Huang, C.P., and Ostovic, F.B. (1978). Removal of Cadmium (II) by Activated Carbon Adsorption. Journal of the Environmental Engineering Division, Proceedings of the American Society of Civil Engineers, 104, pp. 863-878.

Huang, C.P., and Smith, E.H. (1981). Removal of Cadmium (II) from Plating Wastewater by an Activated Carbon Process. In: Chemistry in Water Reuse. 2, Cooper, W.J. (Ed.), Ann Arbor Science Pub., Inc.

Huang, C.P., and Wirth, P.K. (1982). Activated Carbon for Treatment of Cadmium Wastewater. Journal of the Environmental Engineering Division, Proceedings of the American Society of Civil Engineers, 108, pp. 1280-1299.

IARC (1980). International Agency for Research on Cancer. Report of a Working Party. Cancer Research, 40, pp. 1-12 (Quoted by Roberts, 1983).

In Process Pollution Abatement (1973). Upgrading Metal-Finishing Facilities to Reduce Pollution (1). EPA Technology Transfer Seminar Publication.

Interim Effluent Guidance for NPDES Permits. U.S. Environmental Protection Agency, Office of Permit Programs, Washington (Quoted by Besselievre and Schwartz, 1976).

Iyengar, L. (Mrs.) and Rao, A.V.S.P. (1979). Urease Bound to Chitin with Glutoraldehyde. Biotechnology and Bioengineering, 21, 8, p. 1333.

James, R.O., and Healy, T.W. (1972). Adsorption of Hydrolyzable Metal Ions at Oxide-Water Inferface. III. A Thermodynamic Model of Adsorption. Journal of Colloid and Interface Science, 40, pp. 65-81.

Jenkins, S.H., Knight, O.G., and Humpherey, R.E. (1964). The Solubility of Heavy Metal Hydroxide in Water, Sewage, and Sewage Sludge. I. The Solubility of Some Metal Hydroxide. International Journal of Air and Water Pollution, 8, pp. 537-536.

Kobayashi, J. (1971). Relation Between the Itai-Itai Disease and the Pollution of River Water by Cadmium from a Mine. Advances in Water Pollution Research. Proceedings of the Fifth International Conference, San Francisco, Hawaii, Vol. 1, Jenkins, S.H. (Ed.), Pergamon Press, Oxford, London.

Kanwar, K.C., Kaushal, S., and Kumar, R. (1980). Absorption, Distribution, and Excretion of Orally Administered Cadmium in the Rat. Bulletin on Environmental Contamination Toxicology, 24, pp. 321-325.

Labischinski, H., and Naumann, D. (1982). The Three Dimensional Architecture of Bacterial Peptidoglycan: A Comparison with the Conformational Features of Chitin. Proceedings of the Second International Conference on Chitin and Chitosan. Hirano, S., and Tokura, S. (Eds.), The Japanese Society of Chitin and Chitosan, Sapporo, Japan, pp. 93-98.

Lagerwerff, J.V., and Specht, A.W. (1970). Contamination of Roadside Soil and Vegetation with Cadmium, Nickel, Lead and Zinc. Environmental Science and Technology, 4, pp. 583-586.

Lang, E.R., Kienzle-Sterzer, C.A., Rodriguez-Sanchez, D., and Rha, C. (1982). Rheological Behaviour of a Typical Random Coil Polyelectrolyte: Chitosan. Proceedings of the Second International Conference on Chitin and Chitosan. Hirano, S., and Tokura, S. (Eds.), The Japanese Society of Chitin and Chitosan, Sapporo, Japan, pp. 34-38.

Larsen, V.J., and Schierup, H.H. (1981). The Use of Straw for Removal of Heavy Metals from Wastewater. Journal of Environmental Quality, 10, pp. 188-193.

Lauwerys, R. (1979). Cadmium in Man. In: The Chemistry Biochemistry and Biology of Cadmium. Webb, M. (Ed.), Elsevier/North Holland Biomedical Press.

Leckie, J.O., and James, R.O. (1974). Control Mechanisms for Trace Metals in Natural Water. In: Aquatic Environmental Chemistry of Metals. Rubin, A.J. (Ed.), Ann Arbor Science Pub., Inc.

Lemelich, R. (Ed.). (1972). Bubble Separation Techniques. Academic Press, New York.

Linstedt, K.K., Houch, C.P., and O'Connor, J.T. (1971). Trace Element Removal in Advanced Wastewater Treatment Processes. Journal Water Pollution Control Federation, 43, pp. 1057-1513.

Madhavan, P., and Nair, K.G.R. (1978). Metal-Binding Property of Chitosan from Prawn Waste. Proceedings of the First International Conference on Chitin and Chitosan, pp. 444-448.

Manual on Water Supply and Treatment (1976). Central Public Health and Environmental Engineering Organisation, Ministry of Works and Housing, New Delhi.

Masri, M.S., Reuter, F.W., and Friedman, M. (1974). Binding of Metal Cations by Natural Substances. Journal of Applied Polymer Science, 18, pp. 675-681.

Mima, S., Miya, M., Iwamoto, R., and Yoshikawa, S. (1982). Highly Deacetylated Chitin and Its Properties. Proceedings of the Second International Conference on Chitin and Chitosan. Hirano, S., and Tokura, S. (Eds.), The Japanese Society of Chitin and Chitosan, Sapporo, Japan, pp. 21-25.

Muzzarelli, R.A.A. (1977). Chitin. Pergamon, Oxford, pp. 139-150, 215-220 (Quoted by Hirano et.al., 1982).

Muzzarelli, R.A.A., Raith, G., and Tubertini, O. (1970). Separations of Trace Elements from Sea Water, Brine and Sodium and Magnesium Salt Solutions by Chromatography on Chitosan, Journal of Chromatography, 47, pp. 414-420.

Muzzarelli, R.A.A., and Rocchetti, R. (1974). The Use of Chitosan Columns for the Removal of Mercury from Waters. Journal of Chromatography, 96, pp. 115-121.

Muzzarelli, R.A.A., and Rocchetti, R. (1974). Tolanta, 21, p. 1137 (Quoted by Nair and Madhavan, 1982).

Muzzarelli, R.A.A., and Tubertini, O. (1969). Tolanta, 16, p. 1571 (Quoted by Tsezos, 1983).

Nair, K.G.R., and Madhavan, P. (1982). Metal Binding Property of Chitosan from Different Sources. Proceedings of the Second International Conference on Chitin and Chitosan. Hirano, S., and Tokura, S. (Eds.), The Japanese Society of Chitin and Chitosan, Sapporo, Japan.

National Interim Primary Drinking Water Regulations (1976). EPA-570/9-76-003, Office of Water Supply, Washington, D.C.

Nelson, D.J., Kiremidjian-Schumacher, L., and Stotzky, G. (1982). Effects of Cadmium, Lead and Zinc on Macrophage Mediated Cytotoxicity Toward Tumor Cells. Environmental Research, 28, pp. 154-163.

Netzer, A., and Norman, J.D. (1973). Removal of Trace Metals from Wastewater by Activated Carbon. Water Pollution Research in Canada, 8, p. 110 (Quoted by Netzer et.al., 1974).

Netzer, A., Welkinson, P., and Beszedict, S. (1974). Removal of Trace Metal from Wastewater by Treatment with Lime and Discarded Automotive Times. Water Research, 8, pp. 813-817.

Neufeld, R.D., and Hermann, E.R. (1975). Heavy Metal Removal by Acclimated Activated Sludge. Journal Water Pollution Control Federation, 47, pp. 310-330.

Nomiyama, K. (1973). Toxicity of Cadmium-Mechanism and Diagnosis. In: Supplement to Progress in Water Technology. Proceedings of the International Conference held in Nashville Tennessee, Krenkel, P.A. (Ed.), Pergamon Press, Oxford, London.

Nordberg, M. (1978). Studies on Metallothionein and Cadmium. Environmental Research, 15, pp. 381-404.

Page, A.L., and Bingham, F.T. (1973). Cadmium Residue in the Environment. Residue Reviews, 48, pp. 1-43.

Pandey, G.C. (1982). Materials for Metal Pollution Control: Bio-inorganic Study of Some Mercury Complexes. The Journal of Environmental Sciences, pp. 28-31.

Pandey, M.P., and Chaudhuri, M. (1980). Inorganic Mercury-Bituminous Coal Sorption Interaction in Water. Progress in Water Technology, 12, pp. 697-711.

Patterson, J.W. (1975). Wastewater Treatment Technology. Ann Arbor Science Pub., Inc.

Patterson, J.W., Allen, H.E., and Scala, J.J. (1977). Carbonate Precipitation for Heavy Metals Pollutants. Journal Water Pollution Control Federation, 49, pp. 2397-2410.

Patterson, J.W., and Minear, R.A. (1973). Physico-chemical Methods of Heavy Metal Removal. In: Supplement to Progress in Water Technology, Heavy Metals in Aquatic Organisms. Proceedings of the International Conference held in Nashville, Tennessee, Krenkel, P.A. (Ed.), Pergamon Press, Oxford, London.

Peterson, P.J., and Alloway, B.J. (1979). Cadmium in Soil and Vegetation. In: The Chemistry, Biochemistry and Biology of Cadmium. Webb, M. (Ed.), Elsevier/North Holland Biomedical Press.

Randall, J.M., Garrett, V., Bermann, R.L., and Waiss Jr., A.C. (1974). Use of Bark to Remove Heavy Metal Ions from Waste Solutions. Forest Production Journal, 24, pp. 80-84 (Quoted by Larsen and Schierup, 1981).

Randall, J.M., and Hautala, E. (1975). Removal of Heavy Metal Ions from Waste Solutions by Contact with Agricultural Byproducts. Proceedings of the 30th International Waste Conference, Purdue University, Ann Arbor Scienc

Rebhun, S., and Ben-Amotz, A. (1984). The Distribution of Cadmium Between the Marine Algae Chlo Chlorella Stigmatophora and Seawater Medium. Effect on Algal Growth. Water Research, 18, pp. 173-178.

Roberts,P.B. (1983). Interactions Between Cadmium and Radiation in the Killing of Escherichia coli. Environmental Research, 31, 221-228.

Rouse, J.V. (1976). Removal of Heavy Metals from Industrial Effluents. Journal of the Environmental Engineering Division, Proceedings of the American Society of Civil Engineers, 102, pp. 929-936.

Ryan, J.A., Pahren, H.R., and Lucos, J.B. (1982). Controlling Cadmium in the Human Food Chain: A Review and Rationale Based on Health Effects. Environmental Research, 28, pp. 251-302.

Saito, S., Tabeta, R., and Hirano, S. (1982). A High Resolution ^{13}C NMR of Chitin, Chitosan and N-Acyl Chitosans by Cross-Polarization/Magic Angle Spinning (CP/MAS) NMR Spectroscopy. Conformal Behaviour and Gelation Mechanism. Proceedings of the Second International Conference on Chitin and Chitosan. Hirano, S., and Tokura, S. (Eds.), The Japanese Society of Chitin and Chitosan, Sapporo, Japan, pp. 57-62.

Sakaguchi, T., and Nakajima, A. (1982). Recovery of Uranium by Chitin Phosphate and Chitosan Phosphate. Proceedings of the Second International Conference on Chitin and Chitosan. Hirano, S., and Tokura, S. (Eds.), The Japanese Society of Chitin and Chitosan, Sapporo, Japan, pp. 177-182.

Samarawickrama, G.P. (1979). Biological Effects of Cadmium in Mammals. In: The Chemistry, Biochemistry and Biology of Cadmium. Elsevier/North-Holland Biomedical Press.

Seth, P.C., and Pandey, G.S. (1983). Cadmium Spillage through Galvanization Effluents. Indian Journal of Environmental Health, 25, pp. 128-134.

Sephard, B.K., McIntosh, A.W., Atchison, G.J., and Nelson, D.M. (1980). Aspect of Aquatic Chemistry of Cadmium and Zinc in a Heavy Metal Contaminated Lake. Water Research, 14, pp. 1061-1066.

Sommers, L.E. (1977). Chemical Composition of Sewage and Analysis of Their Potential Use as Fertilizers. Journal of Environmental Quality, 6, pp. 225-232.

Sorg, T.J., Csanady, M., and Logsdon, G.S. (1978). Treatment Technology to Meet Interim Primary Drinking Water

Regulations for Inorganics. Part 3. American Water Works Association Journal, 70, pp. 680-691.

Standard Methods for the Examination of Water and Wastewater (1976). (14th ed.). Jointly published by American Water Works Association, American Public Health Association, and Water Pollution Control Federation, New York.

Summary Report (1980). Control and Treatment Technology for the Metal Finishing Industry. Sulfide Precipitation. EPA 625/8-80-003.

Sunderesan, B.B., Bulusu, K.R., Kulkarni, D.N., and Pathak, B.N. (1978). Removal of Iron, Manganese, Copper, Arsenic, Lead, and Cadmium by Serpentine Mineral. Indian Journal of Environmental Health, 20, pp. 413-419.

Travis, C.C., and Etnier, E.L. (1982). Dietary Intake of Cadmium in the United States. Environmental Research, 27, pp. 1-9.

Tsezos, M. (1983). The Role of Chitin in Uranium Adsorption by R. Arrhizus. Biotechnology and Bioengineering, 25, pp. 2025-2040.

Tsezos, M., and Volesky, B. (1982). The Mechanism of Uranium Biosorption by Rhizopus Arrhizus. Biotechnology and Bioengineering, 24, pp. 385-401.

Vaidya, M.V. (Mrs.) and Bulusu, K.R. (1984). Chitosan as Coagulant and Coagulant Aid. Journal of the Institute of Engineers (India), Environmental Engineering Division,

Waste Treatment (1973). Upgrading Metal - Facility to Reduce Pollution. U.S. EPA Technology Transfer.

Weast, C. (Ed.) (1969). Handbook of Chemistry and Physics. (50th ed.), CRC Press, Cleveland, Ohio.

Webber, J. (1972). Effects of Toxic Metals in Sewage on Crops. Water Pollution Control, 71, pp. 404-412.

Webber Jr., W.J. (Ed.) (1972). Physico-chemical Processes for Water and Quality Control. Wiley Interscience, New York.

Weber Jr., W.J., and Possett, H.S. (1974). Equilibrium Models and Precipitation Reactions for Cadmium (II). In: Aqueous Environmental Chemistry of Metals. Rubin, A.J. (Ed.), Ann Arbor Science Pub., Inc.

Wing, R.E. (1974). Heavy Metal Removal from Wastewater with Starch Xanthate. Engineering Bulletin of Purdue University. Proceedings of the 29th Industrial Waste Conference. (Part 1). Engineering Extension Series No. 145.

Wing, R.E., Doane, W.M., and Russell, C.R. (1975). Insoluble Starch Xanthate: Use in Heavy Metal Removal. Journal of Applied Polymer Science, 19, pp. 847-854.

Yaku, F., and Koshijima, T. (1978). Proceedings of the First International Conference on Chitin and Chitosan. pp. 386-404 (Quoted by Hirano et al., 1982).